Second Series. *May, 1915* *Vol. V., No. 5.*

THE

PHYSICAL REVIEW.

THE INFRA-RED TRANSMISSION AND REFLECTION OF A NUMBER OF THE ANILINE DYES.

By J. B. Johnson and B. J. Spence.

IN taking up the study of the infra-red tranmission and reflection of the aniline dyes, there are at least two points open for consideration. First the problem of chemical arrangement and optical properties is by no means solved, but rather in its infancy and any new data which may be added to it, will be of service. For the visible spectrum a large amount of data has been obtained, and a number of interesting conclusions have been drawn from them. On the other hand, for the infra-red spectrum there exists a meagre amount of data in comparison to the amount available and anything like a rigorous test of the theory relating chemical arrangement or constitution with absorption has not been possible.

Unfortunately in studying the infra-red properties one is very much restricted in the study, owing to the great opacity of most of the organic substances to the long wave radiation, consequently leading to the use of very small angled prisms and thin films. Thin films and small angled prisms are in many instances impossible to produce and their use when produced is not at all certain, in the study of the infra-red spectrum.

A second point for consideration in the study of these dyes is their reflecting power. The aniline dyes show the property of surface color to a marked extent and it is possible that this property may exist for other wave lengths than those found in the visible spectrum. Associated with the phenomenon of surface color or residual rays, one finds a weak transmission of the wave lengths so reflected. In considering the subject of metallic reflection it must be borne in mind that not all absorption bands or better, bands of weak transmission, correspond to periods of powerful reflection. The so-called absorption bands are not absorption bands in the true sense, for according to the electro-magnetic theory of light at these wave-lengths the energy does not penetrate into the medium upon which it is incident and give rise to heat (true absorption) but owing to the periodic motion of the electrons set up by the incident vibrations,

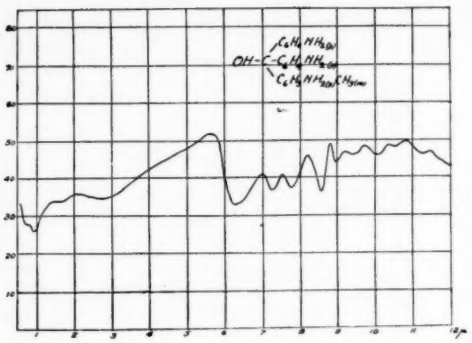

Fig. 1.
Rosaniline.

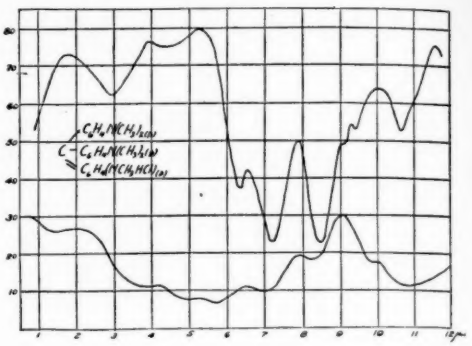

Fig. 2.
Methyl Violet.

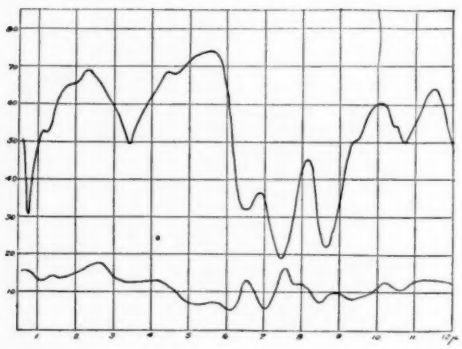

Fig. 3.
Paris Violet.

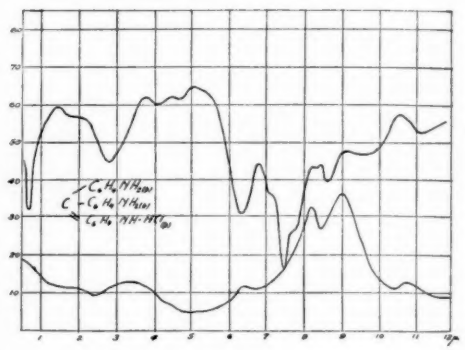

Fig. 4.
Fuchsine.

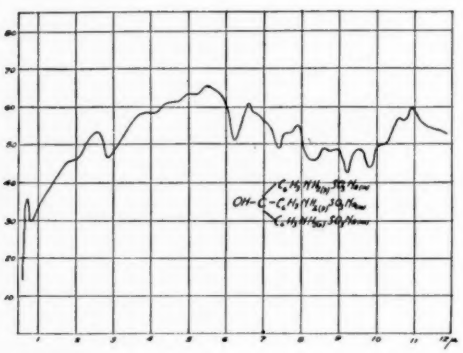

Fig. 5.
Ruby S.

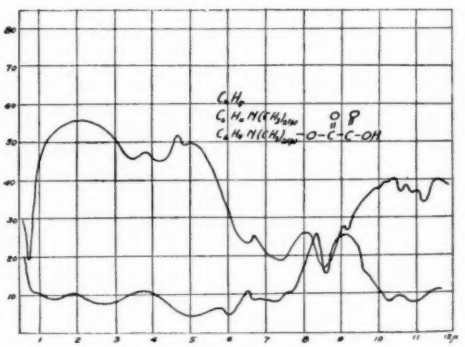

Fig. 6.
Malachite Green.

resulting in a neutralization of the electric intensity at the surface, the energy will be thrust back into the first medium as reflected energy.

A study of the dyes will not therefore be complete until an investigation of their refractive indices can be carried out for the infra-red region. Pfluger[1] has carried out an investigation of the refractive indices and absorption coefficients of the aniline dyes using very small angled prisms. The problem however dealing with the infra-red region is one of considerably more difficulty owing to the strong absorption of the dyes for the longer waves, and the lack of sufficient sensibility of the infra-red spectrometer.

EXPERIMENTAL PROCEDURE.

The investigation was carried on by means of a specially built spectrometer[2] suitable for measurements in the infra-red region of the spectrum. The energy from a Nernst glower was focused upon the slit of the spectrometer by means of a concave mirror. The image of the slit was then brought to focus upon the thermo-pile after having been subjected to the procedure required by the Wadsworth mounting of the rock salt prism.[3]

The thermo-pile galvanometer combination was the same as that previously described by one of us.[4] The combination possessed a sensibility, such that the energy at the position of the sodium lines in the spectrum gave a deflection of 60 mm. with the galvanometer at a distance of a meter and a half from the galvanometer.

In order to determine the transmission of the dye a thin film of it in the solid state was drawn before the slit of the spectrometer by means of a suitable carriage, thus giving a reduced deflection for the desired wavelength. The ratio of the deflection to the deflection without the dye present gave the transmission of the dye for that particular wave length and thickness of the film.

For the determination of the reflection of the dye a modified procedure was necessary. The energy from the glower was focused upon the film of the dye and this image was in turn focused upon the slit of the spectrometer. The film was spread over a piece of glass and fastened to a sliding carriage which also held a piece of silvered mirror. The carriage was so arranged that the dye could be replaced by the polished silver surface. The ratio of the galvanometer deflection with the dye in position to the galvanometer deflection with the silver surface in place gave the percentage reflection.

The chief difficulty experienced in the work was the production of

[1] Wied. Ann., *128*, 145, 1899.

[2] Astrophysical Journal, *39*, 243, 1914.

[3] Phil. Mag., 38, 1904.

[4] *Loc. cit.*

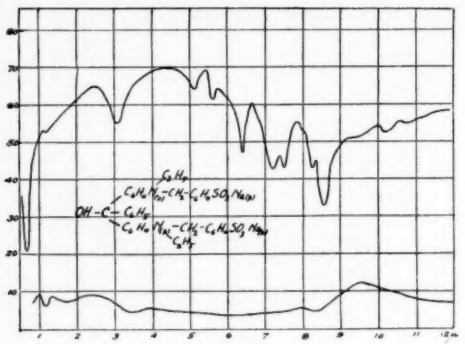

Fig. 7.
Guinea Green.

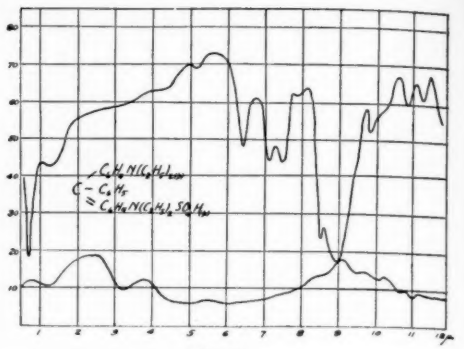

Fig. 8.
Brilliant Green.

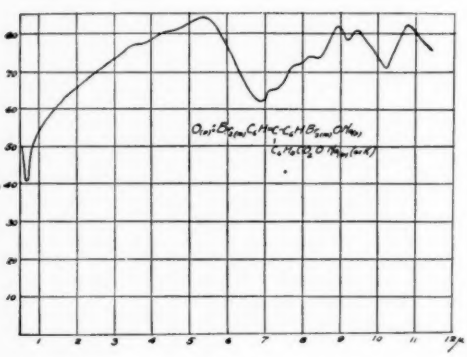

Fig. 9.
Eosine.

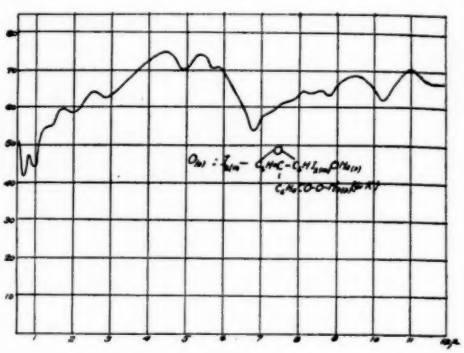

Fig. 10.
Bluish Eosine.

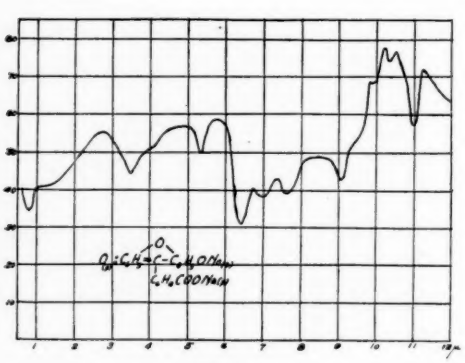

Fig. 11.
Uranine.

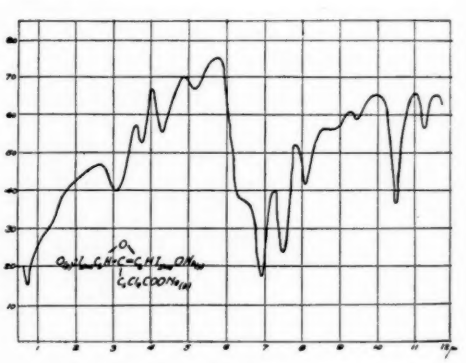

Fig. 12.
Rose Bengal.

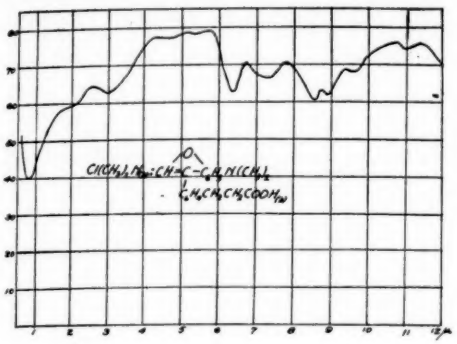

Fig. 13.
Acid Rhodamine.

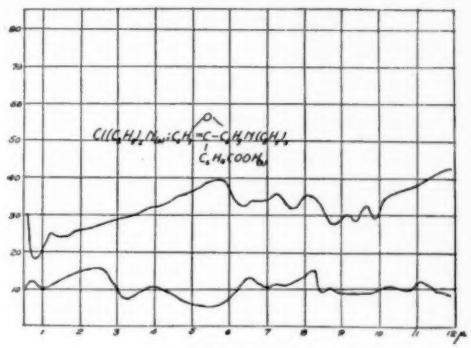

Fig. 14.
Rhodamine.

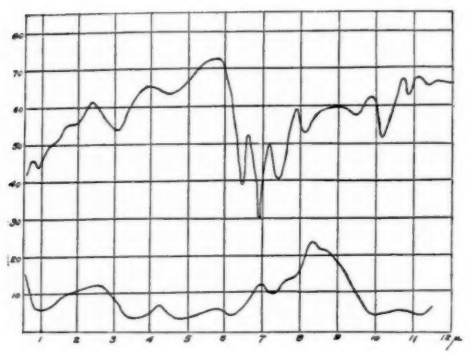

Fig. 15.
Erythrosin.

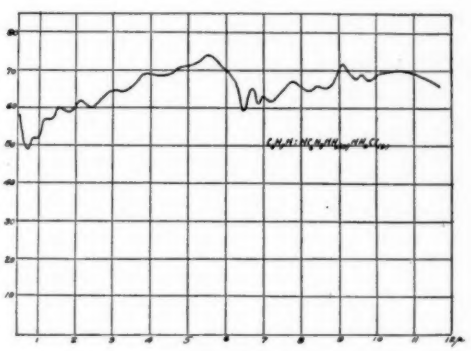

Fig. 16.
Chrysoidine.

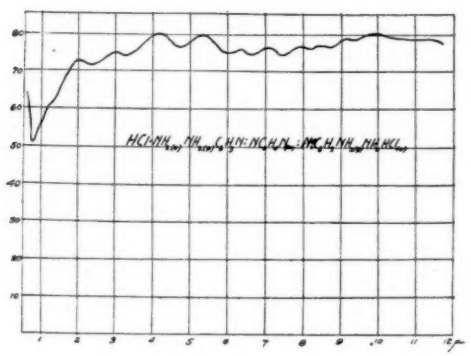

Fig. 17.
Bismarck Brown.

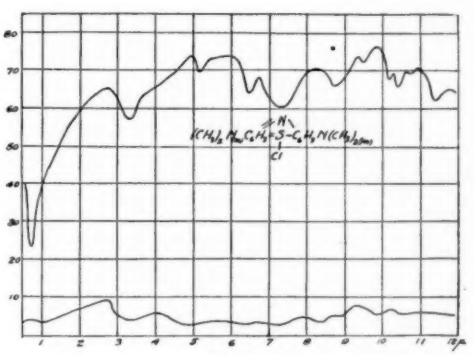

Fig. 18.
Methyl Blue.

suitable films from the dyes. The dyes were so opaque to the infra-red radiation that it was necessary to spread them over the surface of some diathermaneous medium, in this instance rock salt, in very thin films of thickness perhaps not more than a few wave lengths of visible radiation. The use of the rock salt made the production of the films very difficult, in as much as the only good solvent for the dyes is water. It seemed that no regular procedure could be used: each dye required its own particular treatment. In one or two instances a film was formed by melting the dye, but in most instances the films were obtained from solutions formed in amyl alcohol. Frequently, where solution was possible, films could not be obtained owing to the strong surface tension drawing the dyes up into small irregular patches on evaporation of the solvent. The production of films for reflection was in some instances more difficult, for a film which could be used for transmission was frequently too rough for reflection. Consequently it was impossible to obtain the reflection of all the dyes available. Many dyes which could have been used successfully were not available. It is hoped that the future may make these dyes available.

The chemical constitution of the materials was found in Remsen's Organic Chemistry, in Formanek's work and the greatest number in Greene's tables based upon the work of Drs. Shultz and Julius. The constitution of three of the dyes could not be found in the references and of cyanin and æsculin it is only known that they are a quinoline derivative and a glucoside respectively. The constitution of each substance accompanies its transmission curve.

The results are expressed in the form of transmission and reflection curves. The abscissæ are wave-lengths expressed in μ. The ordinates are per cent. transmission and reflection. Where two curves are plotted on the same coördinate system the lower of the two curves is the reflection curve.

The accuracy of the wave-length determination for the transmission curves is about .05 μ with the exception of the wide flat bands of very low transmission where the error is slightly greater. The error for the reflection curves is slightly greater than .05 μ, owing to the small amount of energy reflected corresponding frequently to not more than two or three millimeters galvanometer deflection.

Considering first the transmission curves with reference to the chemical constitution of the substances, a few points of interest are to be noted. There is a general similarity in all of the curves. All have one or two bands in the extreme red end of the visible spectrum causing in part the color of the substance. There is then a region comparatively free from absorption with a maximum of transmission in the region of the wave-

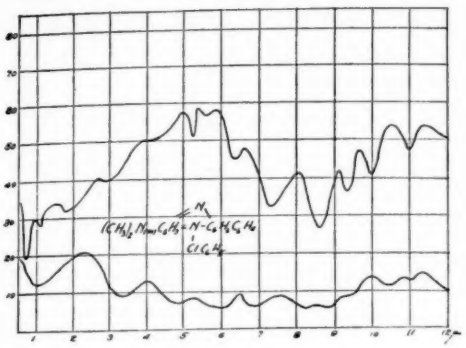

Fig. 19.
Neutral Blue.

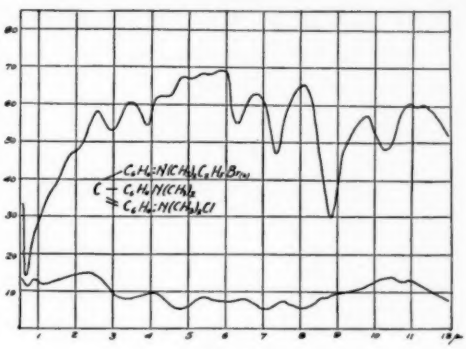

Fig. 20.
Methyl Green.

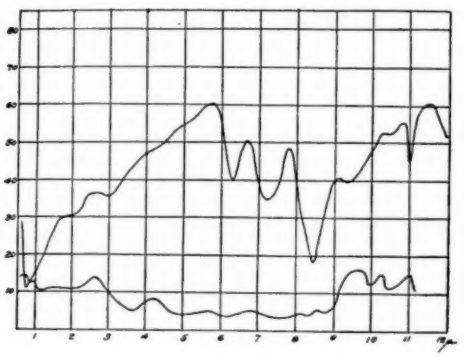

Fig. 21.
Cyanile Green.

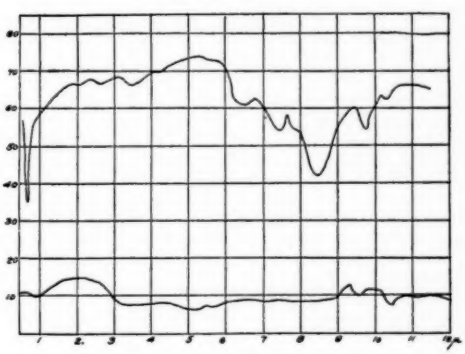

Fig. 22.
Neptune Green.

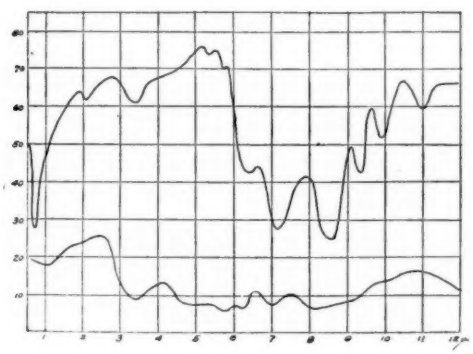

Fig. 23.
Steel Blue.

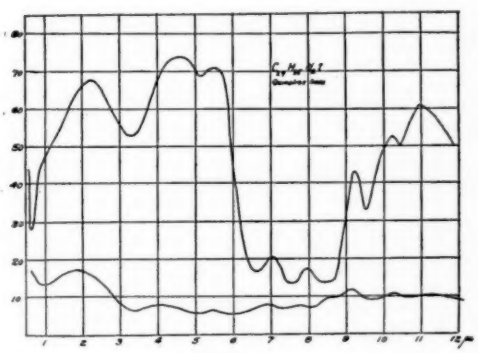

Fig. 24.
Cyanine.

length 5.5 μ. From this point on there is, in most cases, a sudden drop in transmission and then a region of complex absorption takes place to about the wave-length 9.0 μ, where the transmission again increases with or without bands.

In the region of complex absorption before 9.0 μ a higher dispersion would have revealed perhaps a large number of narrow deep bands. Further are to be noted the three deep bands in the interval between 6.0 μ and 9.0 μ of the triphenyl methanes and the triphenyl carbinols, and it would seem that the three substances of unknown composition, cyanile green, neptune green and steel blue, belong to these classes. The rosamine and quinoline substances show bands in this region but less accentuated. The substances named methyl violet and Paris violet are given as identical in composition as is also the case with eosine bluish and erythrosine. Their curves show differences in the disposition of the bands of minimum transmission. This may be due to impurities for it is very difficult to obtain dyes of guaranteed purity, or the differences shown

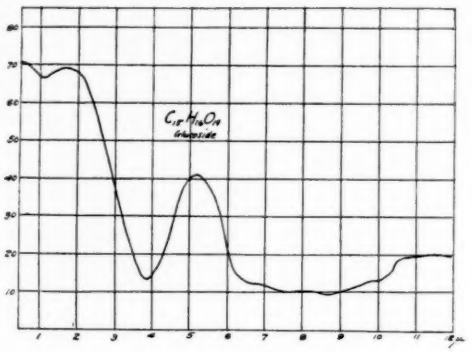

Fig. 25.

Aesculin.

may be in reality due to the differences in chemical arrangement which have not been noted chemically.

Striking differences from the work of other observers appear in the transmission curves. Coblentz gives a list of bands assigned to different groups in the molecule as found by himself and others. The band at 3.42 μ ascribed by Julius to the CH_3 group occurs in but five of the curves, figs. 3, 6, 11, 17 and 24, two of which have the CH_3 group substituted in the amine group, two have no CH_3 groups and the fifth is unknown. The benzene ring is the next most prominent structural feature of these compounds but only two of the curves show a band at 3.25 μ, one has the 6.75 μ band and none the bands at 9.8 μ or 11.8 μ and but few the band at or near the wave-length 8.68 μ.

At least sixteen of the substances contain the OH or the NH_3 groups yet only five curves have the band at 2.95 μ, while none of them have the band at 6.1 μ. On the other hand, acid rhodamine is the only substance examined having the chlorine atom in the ring. It shows the band at 4.30 μ ascribed to chlorine.

From such conflicting data it is difficult to draw conclusions. The theory that certain chemical groups give rise to definite bands of minimum transmission certainly does not appear applicable to such complex substances. The large amount of evidence which seems to support the theory comes largely from a study of substances of fairly simple structure, but even with these substances the theory has a good many qualifications. With the more complex substances various constraints between the groups may well alter the position of the bands corresponding to them. However under these conditions it can not be said that to a certain chemical group there corresponds an absorption band at a definite wave-length.

Reflection.

The reflecting power of the dyes is generally small. The films from which the reflection was obtained were very thin. This should however make no difference in the reflection since the phenomenon sought is a surface one. There is however the possibility that the body color of the dye might make its appearance in the reflection curves but this would be fairly easy to detect for in general the body color obtained from the reflected light would correspond in position with the color shown on transmission.

A study of the reflection curves shows us that in a few instances there is comparatively strong reflection. It however is not of the intensity of metallic reflection. In some instances these maxima correspond to a minimum of transmission. Brilliant green shows a maximum of reflection corresponding to a weak transmission at the wave-length 9.0 μ. Erythrosine shows a maximum of reflection at 6.8 μ corresponding to a sharp minimum of transmission. A further increase of the reflecting power takes place beyond that wave-length corresponding to a rather complicated transmission from which it is difficult to draw definite conclusions. Paris violet shows strong reflection at 6.5 μ and 7.6 μ corresponding to weak transmission. Fuchsine shows a weak maximum of reflection at 6.4 μ corresponding to small transmission. Steel blue shows a broad reflection at the wave-length 8.5 μ corresponding to weak transmission at that point. It is also to be noted that erythrosin possesses a broad band of reflection at 9.4 μ corresponding to complicated transmission. Methyl violet possesses similar characteristics in the region of

10 μ. Likewise malachite green in the region of 9.5 μ. Whether any of the bands of reflection may be classed as residual rays seems rather doubtful, owing to the small value of the reflection coefficient. The method of multiple reflection would in all probability answer the question in the negative. There is one characteristic which nearly all of the dyes show on reflection. One notes on examining the curves that they reflect relatively well to the wave-length 2.8 μ where there occurs a sudden drop to a value of the reflection coefficient of a few per cent. The transmission curves are characterized by a weak transmission at the wave-length 3.0 μ rising to a maximum again rather suddenly. The reflection curves do not rise to a maximum immediately.

CONCLUSIONS.

The reflection and transmission of a number of aniline dyes have been obtained for the infra-red region of the spectrum to the wave-length 12 μ, thus adding more data to the problem of chemical constitution and absorption.

There is a similarity in the transmission curves for related compounds.

The theory that certain chemical groups in the molecule give rise to definite absorption does not hold with any degree of consistency for these complex substances.

The bands of maximum reflection in general coincide with periods of weak transmission. The evidence furnished does not seem to be conclusive in determining whether or not these are bands of metallic reflection. In all probability they are not.

UNIVERSITY OF NORTH DAKOTA,
November, 1914.

NOTE ON THE VALUE OF JOULE-THOMSON OBSERVATIONS FOR COMPUTING STEAM TABLES.

BY HARVEY N. DAVIS.

THIS note is offered for two reasons. In the first place, it is often supposed that Joule-Thomson or throttling experiments are of value chiefly in evaluating the thermodynamic or Kelvin scale of temperature, and in discussions of molecular attraction. As a matter of fact, such observations afford by far the best available means of determining for the use of engineers many of the important thermal properties of such vapors as steam and ammonia. In the case of steam, a point has now been reached where such observations are especially appropriate, since all but one of the remaining gaps can best be filled by this method. In the case of ammonia, much work has still to be done to supply the constants of integration that are necessary in this line of attack, but even here, Joule-Thomson observations will soon be necessary, if the most accurate results are desired.

And in the second place, it is believed that a compact resume of the underlying theory will be useful. In the course of this presentation, the essential identity of certain procedures that have often been regarded as distinct will be pointed out, and a variation of one of them suggested. Furthermore the form of proof presented, although obvious, seems not to have been published.

The fundamental data from which a set of steam tables can be most easily computed are: For the one-phase region, data on (1) the specific heat of superheated steam, and (2) the specific volume of superheated steam. For the two-phase region, data on (3) either the specific volume of saturated steam, or the total heat of saturated steam, or the heat of vaporization, (4) the specific heat of orthobaric water, (5) the specific volume of orthobaric water, and (6) the vapor pressure of wet steam.

Satisfactory data of the fifth and sixth sorts are already at hand. Satisfactory data of the fourth sort are sadly needed, but can hardly be supplied by anything resembling a Joule-Thomson experiment. But everything that is still needed under either of the first three heads, and the outstanding needs are numerous and important, can be supplied better by suitable Joule-Thomson experiments than in any other way.

In the first place, such experiments, if carried out with a heating coil, as suggested by Buckingham in 1903, can yield a direct determination of the specific heat of superheated steam. The heating coil is embedded in the plug of the ordinary experiment, and enables one to put a measured quantity of heat into each gram of steam as it goes through the plug. By this means what would ordinarily be a cooling can be reduced to zero, or changed to a warming of the emerging steam as compared with the entering steam. When the change of temperature is exactly zero, the whole apparatus can be kept at one temperature, and the heat losses of the ordinary sort are zero. It was this advantage that led to the proposal of the plan in the first place. Unfortunately there are heat losses of another sort in the isothermal experiment which, although not as large as in the adiabatic experiment, are more difficult to handle. Nevertheless, let us suppose that the heat losses of both sorts can be controlled, measured and allowed for, and that a series of experiments can be made at different rates of heat input, the high side pressure and temperature and the pressure drop being the same for all. Then if the heat supplied per gram of steam is plotted against the corrected change of temperature (Fig. 1), the result will be a straight line (if c_p is constant within the small

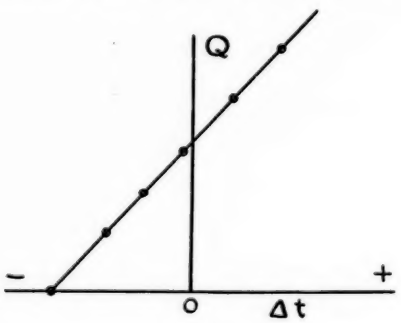

Fig. 1.

temperature range in question) and the slope of this line will be c_p itself for the *low-side* pressure and temperature. To prove this one has only to notice that the plotted curve is really a curve of total heat against actual temperature for various conditions of the low side steam all at the same pressure. Its slope is therefore

$$\left(\frac{\partial H}{\partial t}\right)_p = c_p.$$

Furthermore, since the t-intercept is obviously $\mu\Delta p$, the Q-intercept is $\mu c_p \Delta p$. Whether the inevitable heat losses of various kinds can be eliminated with sufficient accuracy to make this as good a method of

measuring c_p as that of Knoblauch remains to be seen. At any rate, it will afford a useful check, either on c_p, or on the elimination of the heat losses, according to the relative accuracy of the previous knowledge of these two factors.

It should be noticed in passing that this is simply a combination in one experiment of the previously familiar principles of throttling experiments and of continuous flow calorimetry. The less the throttling provided for in designing the plug, the more does this method approach continuous flow calorimetry of the ordinary sort, like that of Knoblauch. But even in his case, where the throttling was made as small as possible, the correction for it is a troublesome one to apply unless it is handled from this point of view. And on the other hand, the introduction of as much throttling as is conveniently possible has the advantages both of helping to ensure that the steam is dry, and of providing twice as great a range of temperature for the specific heat measurements for the same maximum difference of temperature between the steam and its surroundings.

Besides this direct determination of c_p, Joule-Thomson experiments can give indirect but valuable information about c_p, in three substantially equivalent ways proposed originally by Dodge, by Davis and by Grindley. The value of each of these methods lies in the fact that it is easier, especially at high temperatures, to measure c_p at one atmosphere than at higher pressures; for each of these methods enables one to spread a c_p curve, determined at atmospheric pressure, into a family of curves covering as wide a range of pressures as are covered by the Joule-Thomson data. Dodge's and Davis's methods effect this by spreading c_p along lines of constant total heat or enthalpy; Grindley's spreads c_p along lines of constant temperature. The relative convenience of these three methods depends largely on how the Joule-Thomson experiments have been arranged and carried out.

Dodge's method requires that the experiments fall into groups, throughout each of which the high- and low-side pressures are held at fixed values: each group would contain experiments at different and well scattered temperatures. If such data are represented graphically by plotting high-side temperatures as abscissæ and low-side temperatures as ordinates, each group of experiments yields a curve which, at ordinary temperatures, lies below and close to the 45° line of symmetry of the figure, as in Fig. 2. Each point of this curve corresponds to a single experiment in which steam at a high-side temperature t, determined by the abscissa of the point, is throttled into steam at a low-side temperature t_0, determined by the ordinate of the point. Let the high- and low-side pressures corresponding to the whole curve be p and p_0. Then Dodge's

theorem is that the slope of the curve at the given point is equal to the ratio of c_p at (p, t) to c_p at (p_0, t_0). If in each group of experiments, the low-side pressure is one atmosphere, the c_p curve at the high-side pressure is thus determined.

To prove this theorem, let Fig. 3 represent on the p, t plane two experiments corresponding to neighboring points of the curve. In one experi-

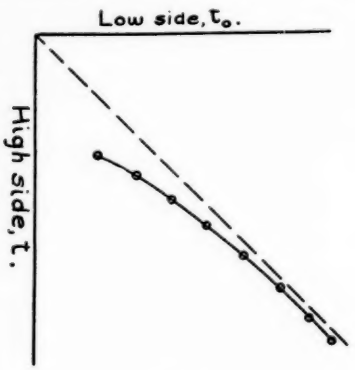

Fig. 2.

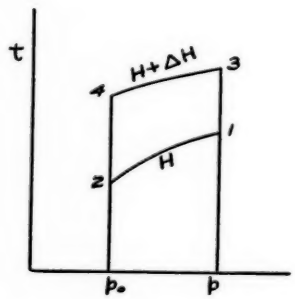

Fig. 3.

ment steam is throttled from state (1) to state (2) with the total heat at the constant value H. In the second experiment steam is throttled from state (3) to state (4) with its total heat at the constant value $H + \Delta H$. At the constant pressure p (line 13), the average value of c_p would be

$$\bar{c}_p = \frac{\Delta H}{t_3 - t_1}.$$

At the constant pressure p_0 (line 24), the average value of c_p would be

$$\bar{c}_{p_0} = \frac{\Delta H}{t_4 - t_2}.$$

So

$$\frac{\bar{c}_p}{\bar{c}_{p_0}} = \frac{t_4 - t_2}{t_3 - t_1}.$$

But in Dodge's figure $(t_4 - t_2)$ would be the difference between the ordinates of neighboring points of the curve, and $(t_3 - t_1)$ would be the difference between their abscissæ. The ratio $\bar{c}_p/\bar{c}_{p_0}$ is therefore equal to the slope of the secant. When ΔH approaches zero, this equation approaches the equation stated in words in Dodge's theorem.

This process is more accurate if modified by the use of the temperature difference $(t_0 - t)$ as ordinate instead of t_0 itself, as in Fig. 4. The curve then lies below and close to the t axis and can be plotted on a much larger

scale. Its slope s for any value of t is now less by unity than before, and

$$\frac{c_p}{c_{p_0}} = 1 + s \quad \text{or} \quad s = \frac{c_p - c_{p_0}}{c_{p_0}} = \frac{\Delta c_p}{c_{p_0}}.$$

That is, the slope, which is now small, is the ratio of the increase in c_p between p_0 and p along a line of constant enthalpy to the value of c_p at the p_0 end of the interval. Since Δc_p is not more than a third of c_{p_0} for any pressure range occuring in ordinary practice, an accuracy of n per

Fig. 4.

cent. in s would give an accuracy of $n/4$ per cent. in the computed c_p even under the most unfavorable circumstances, and a much higher accuracy over a large part of the plane. This offsets, at least in part, the disadvantage of having to use the derivative of an empirically determined function instead of the function itself.

Davis's method is based on a differential equation that can be obtained directly from the modified form of Dodge's equation above. Let $p - p_0$ be called Δp_H. Then

$$\frac{1}{c_p}\left(\frac{\Delta c_p}{\Delta p}\right)_H = \frac{s}{\Delta p_H}.$$

s is the derivative with respect to t at constant p of the function $t_0 - t$, which is the drop of temperature through the plug and is negative. Let this function be called $-\Delta t_H$, so that a positive Δt may correspond to a rise of temperature as usual. Then

$$\frac{s}{\Delta p_H} = -\frac{1}{\Delta p_H}\frac{\partial}{\partial t_p}(\Delta t)_H = -\frac{\partial}{\partial t_p}\left(\frac{\Delta t}{\Delta p}\right)_H.$$

If now Δp_H approaches zero, this difference equation becomes

$$\frac{1}{c_p}\left(\frac{\partial c_p}{\partial p}\right)_H = -\left(\frac{\partial \mu}{\partial t}\right)_p,$$

where μ is the Joule-Thomson coefficient, and is the limit approached by $(\Delta t/\Delta p)_H$. This is Davis's differential equation.[1] Its integral is

$$c_p = c_{p_0} e^{-\int_{p_0}^{p}\left(\frac{\partial \mu}{\partial t}\right)_p dp},$$

the integration being at constant H. When μ is known as a function of

[1] For other proofs of this equation see Davis, Proc. Am. Acad., 45, 1910, p. 291.

p and t, the integration can be effected by mechanical quadrature, and the ratio c_p/c_{p_0} determined. The chief advantage of Dodge's method over this is that, in Dodge's method, the integration is performed automatically by the steam itself for the pressure range covered by a set of experiments.

Grindley's method is based on a differential equation that can be deduced directly from this one. According to a familiar transformation formula,

$$\left(\frac{\partial c_p}{\partial p}\right)_H = \left(\frac{\partial c_p}{\partial p}\right)_t + \left(\frac{\partial c_p}{\partial t}\right)_p \left(\frac{\partial t}{\partial p}\right)_H = \left(\frac{\partial c_p}{\partial p}\right)_t + \mu \left(\frac{\partial c_p}{\partial t}\right)_p.$$

Therefore the last equation becomes

$$\left(\frac{\partial c_p}{\partial p}\right)_t = -\mu \left(\frac{\partial c_p}{\partial t}\right)_p - c_p \left(\frac{\partial \mu}{\partial t}\right)_p = -\left[\frac{\partial(\mu c_p)}{\partial t}\right]_p.$$

This is Grindley's equation. Its integral is

$$c_p - c_{p_0} = \Delta_t c_p = -\int_{p_0}^{p} \left[\frac{\partial(\mu c_p)}{\partial t}\right]_p dp.$$

this integration being at constant temperature.

This equation has certain advantages over that proposed by Davis. Thus it spreads c_p along lines of constant temperature instead of along lines of constant enthalpy, which is more convenient. It also determines the increment in c_p instead of a ratio, which is conducive to accuracy. And finally it involves the product μc_p instead of μ alone. Whether this is an advantage or a disadvantage depends on whether the isothermal or the adiabatic plug experiment can be carried out with greater accuracy.

It is at very high superheats that all three of these methods are most useful, because, under these circumstances, other methods of getting c_p are facing their greatest difficulties. Thus, while the experiments of Knoblauch determine the spacing of the c_p curves at different pressures with much accuracy at moderate temperatures, they fail entirely to separate these curves at and above 500° C., the experimental points at the various pressures being inextricably mixed. Even the roughest sort of knowledge of μ in this region would space the curves more satisfactorily, after the experiments had determined the average height at which they should lie.

Whether Grindley's or Davis's equation will prove to be more useful at high superheats will depend on whether μ or the product μc_p comes nearer to following a law of corresponding states. It has frequently been assumed that μ follows such a law.[1] If so, Davis's equation is the

[1] For instance, by Buckingham, by Berthelot, by Callendar, and by Davis.

useful one. But μ is essentially a calorimetric quantity, and if it does follow a law of corresponding states, it is the only calorimetric quantity known to do so. The product μc_p on the other hand is a specific volume, and it was for specific volumes that the law of corresponding states was originally proposed. One would therefore have predicted *a priori* that the product μc_p would be more amenable to such treatment than μ. If so, Grindley's equation is the useful one.

Turning now to the specific volume of superheated steam, we have the well known relation

$$\frac{v}{T} = \frac{v_0}{T_0} + \int_{T_0}^{T} \frac{\mu c_p}{T^2}\, dT,$$

where the integration is to be carried out at constant pressure. For a perfect gas, μ would be zero, the integral would vanish, and v would be proportional to T at constant pressure. For steam, the integral appears as a small correction term on the ratio v/T. v can therefore be computed as a function of T along an isopiestic, if its value is known at any one point of the isopiestic. Fortunately v is known close to the saturation line from computations with the Clapyron equation, and from the experiments of Knoblauch, Linde and Klebe. This gives a starting point for every isopiestic between 1 and 10 atmospheres. Within this pressure range, the best way to get specific volumes at any temperature however high is undoubtedly to make measurements, not on v itself, but on the product μc_p.

This procedure has certain great advantages. In particular, the object of the experiments is to determine, not the whole quantity sought, but a relatively small correction term. For example, in computing the specific volume of steam at 50 lbs. per sq. in. abs. and 600° F. superheat, the whole correction term is probably not more than 5 per cent. of the answer sought. If, therefore, the correction term is known within 2 per cent. of itself, the specific volume is known within 0.1 per cent. of itself, which is as good as the accuracy of the initial volume used as the constant of integration. Furthermore, the correction term is not an observed quantity but the integral of an observed quantity. The only chance for a 2 per cent. error in the integral is a *systematic* error in μc_p amounting to 2 per cent. throughout the whole range. The allowable *accidental* errors in μc_p might be considerably greater than 2 per cent. for an accuracy of 0.1 per cent. in v.

Let us now turn to saturated and wet steam. It is almost certain that suitable Joule-Thomson experiments with superheated steam can be made to yield a more accurate determination of the *shape* of the *HT* curve of saturated steam than can be obtained in any other way.[1]

[1] See Davis, Proc. Am. Acad., *45*, 272, 1910.

Briefly, the fundamental principle is that if, by means of throttling experiments, we can plot the lines of constant H on the superheated steam plane, and if, by means of c_p values, for any one pressure, we can determine the differences ΔH from each curve to the next, we have a determination of the increase in H along the saturation line for each interval between points of intersection with our curves. If H is known by direct measurement at any one point of the saturation line, this process will give its value all along the line. Fortunately there are a number of good determinations of H between 0° C. and 160° C., particularly near 100° C. A good set of Joule-Thomson experiments is therefore all that is needed to determine a satisfactory HT curve over a considerable range.

This process, like that for computing the v of superheated steam, has the great advantage of concentrating the efforts of the experimenter, not on the whole quantity sought, but on a comparatively small increment term. Thus if H_{100} is assumed to be known, the term to be determined experimentally is never greater than 5 per cent. of H itself, and 1 per cent. on the correction term gives 0.05 per cent. on H, which is somewhat better than the accuracy of our present knowledge of H at the boiling point.

When the H curve is thus determined, it will be easy to compute the specific volume of saturated steam by means of the Clapyron equation, if only the specific heat of water and the vapor pressure curve are known. The latter is now well known over the whole range from 0° C. to the critical point, but our knowledge of the specific heat of water is very meager at high temperatures and very chaotic at ordinary temperatures.

Finally, when all these things have been computed, either from the satisfactory data already in hand or from a good set of Joule-Thomson data, an interesting check on the self-consistency of the whole steam table is afforded by Planck's equation

$$c_p = \frac{dH_{\text{sat}}}{dt} - \frac{L}{T} + T\left(\frac{dp}{dt}\right)\left[\left(\frac{\partial v}{\partial t}\right)_{p_{\text{steam}}} - \left(\frac{\partial v}{\partial t}\right)_{p_{\text{liquid}}}\right],$$

where L is the latent heat at the temperature in question. The derivatives in the last term refer to superheated steam and water close to, but not inside, the steam dome. The c_p thus computed is the limiting value on the saturation line approached by the c_p of superheated steam. The fundamental data from which the right hand side can be computed are (1) the value of $(dp/dt)_{\text{sat}}$, which is well known, (2) the value of L or H at 100° C., which is fairly well known, (3) a knowledge of the variations of L and H with temperature, which should depend chiefly on Joule-Thomson data, and (4) the value of $(\partial v/\partial t)_p$ for steam, which also should

depend chiefly on Joule-Thomson data. The derivative for water is practically negligible. It is true that a knowledge of c_p itself, which is the quantity sought, is involved in the computation of the variation of L or H with temperature, but it happens that this indirect dependence of the right hand side on c_p is such as to make the computation insensitive to errors in the values of c_p originally assumed. The equation therefore affords a valuable method of successive approximations for computing c_p along the saturation line, where direct measurements are most difficult, as well as a useful check on the c_p curves in general.

It appears, then, that the only experiments that are now greatly needed to put our steam tables on a thoroughly satisfactory basis are a complete and accurate series of Joule-Thomson or throttling experiments, and a thoroughly satisfactory series of experiments on the specific heat of water, especially at high temperatures. Both sorts of experiments are now in progress in the Jefferson Physical Laboratory, and, I believe, elsewhere as well, and it is hoped that the results will be sufficient to serve the purposes which have been indicated.

JEFFERSON PHYSICAL LABORATORY,
CAMBRIDGE, MASS., Jan., 1915.

THE RESULT OF PLOTTING THE SEPARATION OF HOMOLOGOUS PAIRS AGAINST ATOMIC NUMBERS INSTEAD OF ATOMIC WEIGHTS.

BY HERBERT E. IVES AND OTTO STUHLMANN, JR.

THE relationship between the characteristic spectra of the chemical elements and their atomic weights and chemical properties has been the subject of considerable study. Ramage,[1] Runge and Precht,[2] Watts[3] and Rudorf[4] may be mentioned among those who have sought for and established more or less definite connections between the frequencies of spectrum lines and atomic weights. In every case however there have been exceptions and discrepancies of such character as to indicate that while there is undoubtedly a real connection the true relationship has not been found.

Perhaps the most interesting contribution to this problem was furnished by Runge and Precht, in their attempt to determine the atomic weight of radium from spectroscopic evidence. They stated the following law: "In each group of chemically related elements the atomic weight varies as some power of the distance apart of the two lines of a pair," so that "the logarithms of the atomic weights and those of the distances when plotted as coördinates lie on a straight line for a chemically related group of elements." They are careful to apply this law only to "homologous" pairs of lines; homologous lines being characterized by similar behavior in the magnetic field.

Having established the generality of this law Runge and Precht applied it to the group of elements, magnesium, calcium, strontium, barium, radium. Extrapolating for the latter element they obtained a value of 257.8, which disagreed by 13 per cent. from the value obtained by Mme. Curie by chemical methods. Runge and Precht point out that the Curie value may be expected to be too low by reason of the effect of impurities. Nevertheless the high value obtained by them is generally considered incompatible with the place of radium in the periodic system and the spectroscopic method is to some extent discredited.

[1] Proc. Royal Society, LXX., p. 3, 1901.
[2] Phil. Mag. (5), 476, 1903.
[3] Phil. Mag., July 1903, August, 1904.
[4] Zeits. Phys. Chemie, 50, p. 100, 1904.

The spectroscopic value would probably be entitled to more consideration were it not for the fact that other exceptions than radium were found to the law. The existence of exceptions of course detracts seriously from the applicability of any rule for purposes of prophesy. Thus boron and potassium were noted by Runge and Precht. With regard to boron they remark that it had not been examined in a magnetic field so that their choice of lines might be at fault. In regard to potassium the follow-

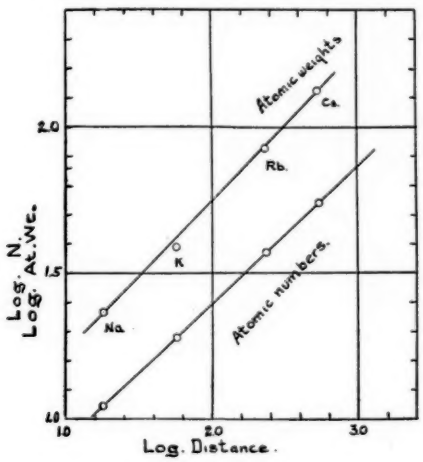

Fig. 1.

ing highly significant remark is made: "It appears to us interesting that the straight line law is appreciably departed from precisely in the case of the element whose atomic weight in the periodic system points to an unknown disturbing cause, which produces the inversion of the positions of argon and potassium."

Within the past year it has been strikingly demonstrated by the work of Mosely[1] that the most characteristic figure connected with a chemical element is not its atomic weight, but its *atomic number*, which is identified with the charge on the positive nucleus of the Rutherford atom. Not only are these atomic numbers whole numbers but the various elements follow each other in the order of their chemical properties without the inversions found in the cases of nickel and cobalt, argon and potassium, tellurium and iodine, when atomic weights are considered. The periodic system should apparently be built around atomic numbers, not atomic weights.

It occurred to us that the problem of the relation between chemical properties and spectroscopic phenomena might be assisted by recourse

[1] Phil. Mag., *27*, p. 703, 1914.

to the newer reference frame. We have therefore re-plotted the figures used by Runge and Precht, with interesting results.

In Fig. 1 we have plotted the series sodium, potassium, rubidium, cæsium, both in terms of atomic weights and atomic numbers. It is at once clear that the "unknown disturbing cause" is the use of the non-significant atomic weight, for on the atomic number plot potassium is no longer an exception to the straight-line relationship.

In Fig. 2 is shown the series in which boron occurs. It too falls in line.

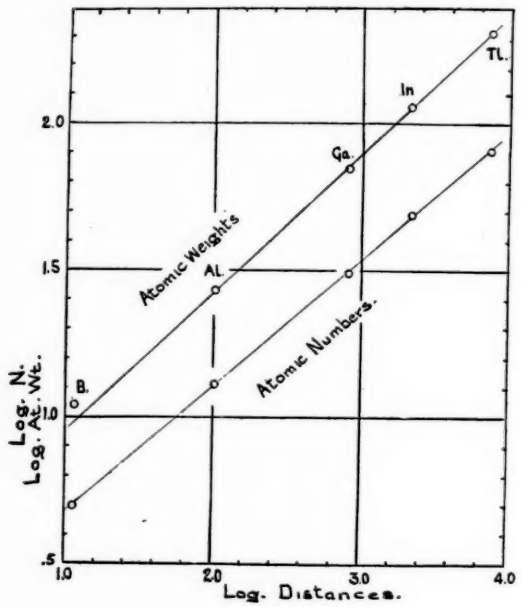

Fig. 2.

The data of these two figures were taken from the paper by Runge and Precht, and apply to lines which fulfill their criterion as to homologous character. Another exception to the law is pointed out by Rudorf, in the series zinc, cadmium, mercury. Upon plotting his data,[1] as we have done in Fig. 3, it appears probable that the reason for this exception is again the choice of atomic weights instead of atomic numbers, for the atomic number points fall on a straight line.

What happens when we attempt to obtain the atomic number of radium by this revised law? Fig. 4 shows the series from magnesium to radium, using again the data of Runge and Precht. Calcium, barium and strontium fall on a straight line, but magnesium falls slightly off. (The atomic number 13 would fit the case better than the number 12

[1] Rudorf, loc. cit., p. 101.

which has been ascribed to this element.) Continuing the line through the calcium, barium, strontium group we obtain for radium the number 96. The atomic number ascribed to radium is actually 88.

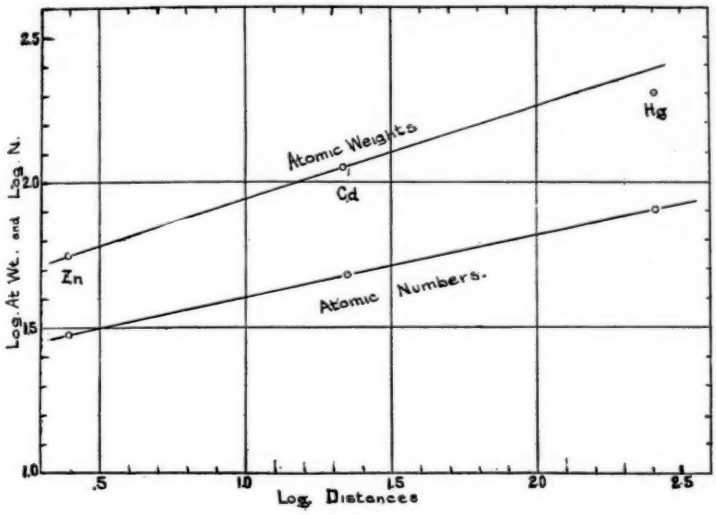

Fig. 3.

It appears, therefore, that while the exceptions which previously cast doubt on this relationship have been eliminated by the new method of

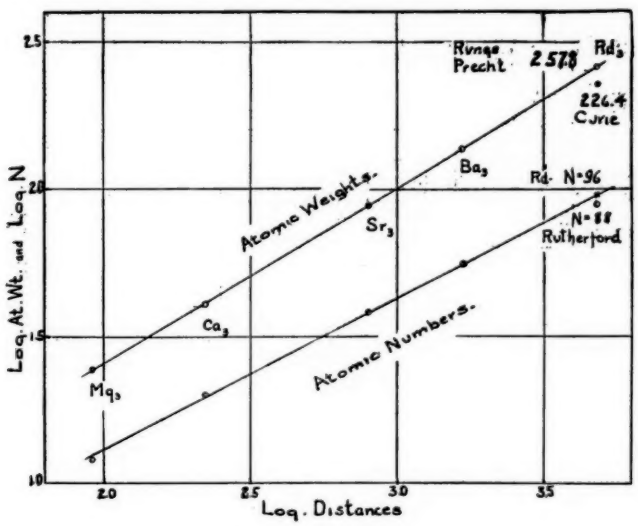

Fig. 4.

plotting, the best it can do for radium is to reduce the discrepancy from 13 to 8 per cent., at the same time getting into trouble with magnesium.

Against this, however, may be set the fact that the atomic number of radium has been derived only indirectly through its relationship to lead, and that of magnesium has not been experimentally determined. At any rate the relationship between line separation and atomic number is so very satisfactory in the case of the other groups of elements as to suggest the desirability of going over anew the experimental work on which the data depend in the magnesium-radium group.

It is of course obvious that this entirely empirical relationship must be, if true, a necessary consequence of the complete mathematical description of the structure of the atom. The fact that it is apparently a function of atomic numbers, on which the most recent picture of the atom is built, gives, we believe, some slight additional support to the idea of the nucleus atom. At the same time it suggests that a review of outstanding difficulties both in the periodic system and in series relations in spectra, might be undertaken with atomic numbers as a basis, with profitable results.

PHYSICAL LABORATORY, THE UNITED GAS IMPROVEMENT COMPANY.
RANDALL MORGAN LABORATORY OF PHYSICS, UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, PA., January, 1915.

THE CHANGE IN THE ELASTICITY OF A MILD STEEL WIRE WITH CURRENT AND EXTERNAL HEATING.

BY H. L. DODGE.

THE effect of current and external heating upon the Young's modulus of a copper wire was described in a previous number of the PHYSICAL REVIEW.[1] The present paper deals with a similar investigation of a mild steel wire, the more marked changes being an increased temperature range, namely 20° C. to 475° C., and slightly greater accuracy. For a detailed description of the apparatus and method of making the determinations the former paper should be consulted.

IMPROVEMENTS IN APPARATUS AND METHOD.

Mention cannot however be omitted of certain changes which have resulted in greater accuracy. Attention was called in the previous paper to the desirability of having the specimen of wire free from mechanical interference between the two points of suspension. The only interference in the case of copper wire was the three thermo-couples of fine wire which did not seem to cause any inaccuracy in the results. Some changes in the method of measuring the temperature have made these unnecessary and in the present apparatus the specimen of wire hangs absolutely free.

As before, the temperature of the wire is determined by its change in length with increase of temperature. In the former paper the justification and advantages of this method were explained. The same statements apply in the present instance as the only changes have been in the process of finding the relation between temperature and length. This was found as follows:

A thermo-couple was carefully calibrated by means of a thermometer. It was then attached to the wire at the middle point and the relation between the temperature of this point and the length determined. As all the points of the wire were not at the same temperature it was necessary to find the relation between the average temperature and the temperature of the middle point. The heating box was maintained at a constant temperature of about 350° C. and a large number of thermo-couple readings taken at various points on the wire. This not only

[1] PHYS. REV., N. S., Vol. 2, 431, 1913.

established the relation between the average temperature of the wire and its length but also gave complete information concerning the temperature distribution. Under the above conditions the maximum variation of the temperature along the wire was about 40° C. while the error in the measurement of the average temperature was probably not more than 10° C. At lower temperatures the accuracy is of course greater, the error amounting to but one or two degrees at or near room temperature and perhaps five degrees at 150° C. At higher temperatures the possibility of error is of course greater amounting to about 20° C. at 475° C. The curve representing the relation between change of length and temperature was plotted and found to be a straight line within the limits of accuracy of the temperature measurements. The increase in length between 20° C. and 475° C., corrected for the stretch caused by the decrease in the modulus, was 3.67 mm. As the wire was 57.6 cm. between points of observation the mean temperature coefficient of expansion proves to be .000014 with a possible error of five per cent.

Considerably increased accuracy has been secured in the measurement of the stretch and consequently the modulus with the present apparatus by the use of new microscopes and micrometer slides with screws accurate to .001 mm.

THE SPECIMEN.

The sample of wire upon which the tests were made was obtained from the Driver-Harris Wire Co., Harrison, N. J. A chemical analysis of the wire secured from Mr. J. W. Whitfield of the firm of Booth, Garrett and Blair, Philadelphia, Pa., was as follows: Silicon, 0.057 per cent.; sulphur, 0.059 per cent.; phosphorus, 0.105 per cent.; manganese, 0.735 per cent.; carbon, 0.162 per cent.; iron (by differences), 98.882 per cent. The sample was pronounced a " mild " or low carbon steel.

The mean coefficient of expansion between 20° C. and 475° C. is 14×10^{-6} per degree Centigrade to an accuracy of about five per cent. The wire is .82 mm. in diameter. The portion between the points of observation was 57.6 cm. long. A weight of 2,109 grams was kept upon the wire continually, the modulus being determined by measuring the elongation produced by an additional weight of 2,252 grams. Certain additional facts regarding the loading, current, number of readings, time between readings, duration of tests, etc., appear in Table I. which contains the complete data of a characteristic series of observations with current heating. The other series differ materially only in method of heating or temperature range.

NATURE OF THE TESTS.

The preliminary observations made while the wire was being straightened and brought to a cyclic state revealed striking irregularities in its behavior. At first increase of temperature increased the modulus but this effect soon disappeared. Continued heating and testing gradually increased the modulus. This was probably due largely to stretching and straightening. Both current and external heating were employed and no effect characteristic of the method of heating could be detected. After a number of cycles of heating and cooling accompanied by stretching, the wire was brought to a cyclic state and the more extended tests made.

The first group of observations were with a temperature range of 20° C. to 300° C. The tests were with both external and internal heating and increasing and decreasing temperature and were so arranged as to reveal if possible any effects peculiar to the method of heating or the thermal route by which any temperature was reached. Later the temperature range was extended to 450° C. and to 475° C. and similar series of tests made. A few characteristic results are shown in Figs. 1, 2 and 3, explanations of which follow.

EXPLANATIONS OF THE CURVES.

Figs. 1, 2 and 3 represent graphically certain of the results that have been obtained. Table I. contains the complete data for series 19, Fig. 2. The data for the other curves do not differ materially in general character. In every case the dotted points represent determinations of the modulus with increasing temperature and the crosses those with decreasing temperature. Nearly all the points are the result of ten or more observations. When the terms " external " and " internal " heating are employed the former indicates that the wire was heated by means of a heating element of nichrome wire extending along the bottom of the enclosing box, while the latter term refers to heating by means of an electric current passing through the specimen itself.

In all of the statements regarding the absence of certain effects it should be understood that this refers to effects amounting to one per cent. or more. The present apparatus cannot detect variations in the modulus of a less amount. The accuracy of the work can best be judged from the curves. A change in the modulus of as much as ten per cent. corresponds to a difference in stretch of only 0.013 mm.

The first four series covered a temperature range of 20° C. to 300° C. with both external and internal heating and showed a practically linear relation between Young's modulus and temperature. Series 5, Fig. 1,

was with external heating, increasing and decreasing temperature. Series 6 and 8 are plotted together. They were with internal heating, increasing and decreasing temperature. The results of the first eight series show that for temperatures below 300° C. the elasticity is a definite function of temperature, independent of manner of heating and free from any hysteresis effects.

It was next thought desirable to extend the temperature range by a considerable amount and to repeat the tests in various orders to ascertain whether the same relations hold for a greater range of temperature. Upon heating above 300° C. a very rapid decrease of the modulus was discovered, the rate of decrease becoming very marked at about 450° C. The results are shown in Fig. 1, series 9. At this temperature the wire

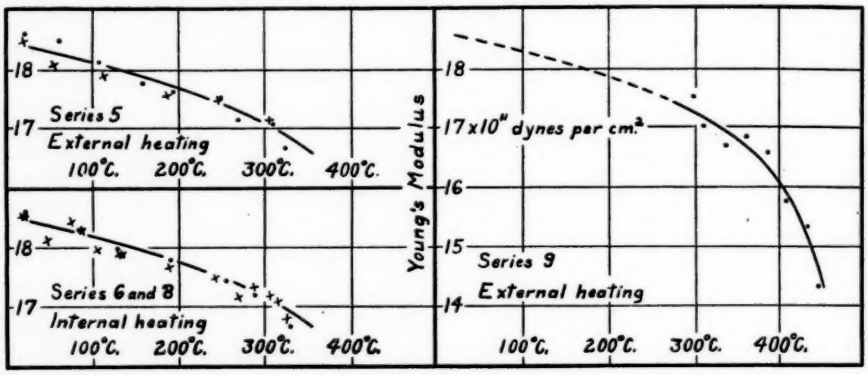

Fig. 1.

Change of Young's modulus of a mild steel wire with temperature.

stretched about one fourth of a millimeter, approximately .05 per cent. of its length. When the elastic limit is exceeded there should be an increase of the modulus for all temperatures. The next observation at room temperature showed an increase from 18.5 to 19.2 or 2.6 per cent. The increase of the modulus for other temperatures as well can be seen from Fig. 2.

The first three series of observations of Fig. 2 give the temperature variation of Young's modulus with external heating. Series 11 shows the type of curve, and the return of the modulus to the same value after a day of heating and stretching. Series 12 was taken under similar conditions. By yielding the same results it proves the total disappearance of all history effects except the very gradual increase of the modulus with continued heating and stretching. As the observations for decreasing temperature in the last two series were few, series 13 was made in order to learn whether the curve with decreasing temperature is the same as

with increasing temperature. The results indicate the absence of any hysteresis effect. In order that the various series in this and the other figures may be more easily compared the curve which appears was drawn to fit a composite of them all. Its shape is exactly the same in every case

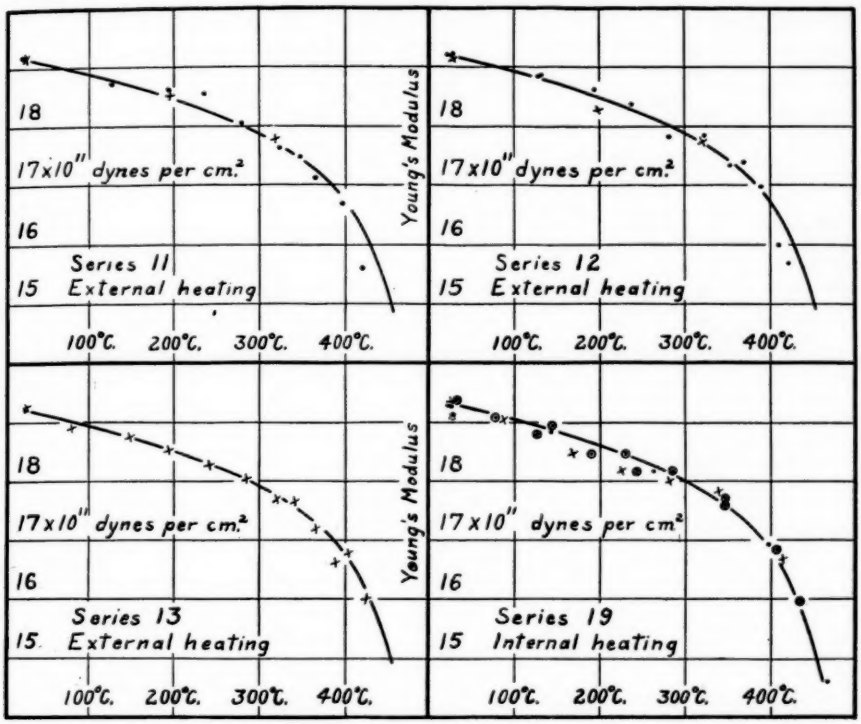

Fig. 2.

Change of Young's modulus of a mild steel wire with increasing and decreasing temperature and with internal and external heating.

the only difference being that it is gradually raised to correspond to the general increase of the modulus as the work progressed.

All of the observations so far had been made with the wire enclosed in an asbestos board heating box so that the currents used in the wire and the heating element might be as low as possible. Walker[1] has found a great difference between the effects of internal and external heating, dependent in part upon the current density. He interprets these results as caused by the magnetic effect of the current, the maximum field which he secures having an average value of 31 gausses.

When series 19 (see Table I.) was taken an attempt was made to find this effect in case it were associated with residual magnetism. Between

[1] Proc. Roy. Soc. Edin., Vol. 31, 186, 1910.

the first two observations of this series (Fig. 2) the wire was subjected for an instant to a current corresponding to an average field of 50 gausses. The difference in the two plotted points is but a fraction of the experi-

TABLE I.

Data for Series 19, Internal Heating.

Length of wire ..... 57.6 cm.
Diameter of wire ..... .82 mm.
Unvarying load ..... 2109 g.
Added load ..... 2252 g.
Total load per sq. mm ..... 8.2 kg.

Obs. No.	Time.	Temp.	Stretch.	Current.	No. of Obs.	Young's Modulus $\times 10^{-11}$ Dynes per Cm.^{2}
1	9:30 A.M.	22° C.	.1250 mm.	0.0 amp.	12	19.3
2	10:00	24	.1250	0.0	10	19.3
3	10:20	142	.1280	5.7	10	18.9
4	10:55	263	.1325	7.4	10	18.2
5	11:35	398	.1425	8.5	11	16.9
6	11:50	466	.1650	9.0	5	14.6
7	12:50 P.M.	416	.1445	8.5	10	16.7
8	1:20	340	.1350	7.9	12	17.8
9	2:00	282	.1340	7.4	11	18.0
10	2:45	224	.1325	6.8	11	18.2
11	3:30	168	.1305	6.0	10	18.5
12	4:00	86	.1265	4.0	10	19.1
13	5:00	26	.1240	0.0	11	19.4
14	5:25	77	.1265	3.8	10	19.1
15	5:50	144	.1270	5.6	11	19.0
16	6:50	188	.1305	6.4	10	18.5
17	7:30	230	.1305	7.0	10	18.5
18	7:55	284	.1325	7.6	11	18.2
19	8:20	384	.1360	8.2	11	17.7
20	8:45	408	.1430	8.5	14	16.8
21	9:05	434	.1560	8.7	10	16.0
22	9:30	346	.1370	8.0	11	17.6
23	9:55	244	.1325	7.0	11	18.2
24	10:30	128	.1280	5.0	12	18.8
25	11:00	28	.1240	0.0	10	19.4

mental error. Neither this test nor any of the other results up to this time gave any suggestion of the effects Walker reports.

It seemed desirable however to employ as large currents as possible in an attempt to bring out the effect. Accordingly the cover of the box enclosing the wire was removed giving the air free access. Series 21, Fig. 3, is the result, the maximum current being 9 amperes, corresponding to a current density of 17 amperes per square millimeter and an average field of 29 gausses. For purposes of comparison series 22 was taken with

external heating, the slight tendency of the readings to fall lower (less than .001 mm. difference in the actual measurements) being probably due entirely to the experimental errors caused by the fact that the main

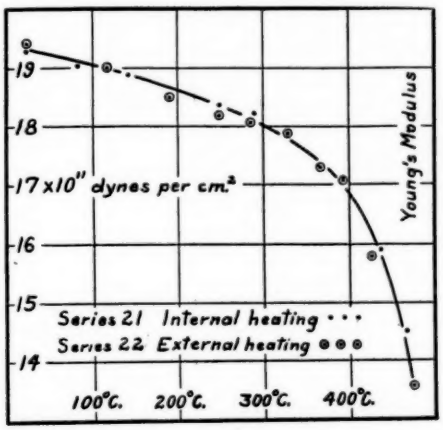

Fig. 3.

Results with internal heating, using the largest possible currents, compared with those with external heating.

part of the apparatus was much hotter in the latter case. No indication of the effects reported by Walker is to be found.

COMPARISON WITH THE RESULTS OF OTHERS.

The earlier work[1] upon the effect of an electric current upon Young's modulus is of very questionable value. Reference will be made only to the more recent work of Walker and Miss Noyes. Miss Noyes[2] found no effect peculiar to current in the case of piano wire but her work was not of sufficient accuracy to have revealed even a relatively large difference. Walker,[3] on the other hand, taking measurements with what appears to be a considerably greater accuracy found striking differences of large magnitude. There are several points concerning even his most recent work that make one seriously question whether the results which he secured are attributable to the causes to which they are assigned. A lengthy discussion of Walker's work is out of place at this time but two or three differences in our results may be of interest.

Walker worked over a temperature range of 20° C. to 125° C., finding in the case of iron wire a maximum value of the modulus at about 50° C.,

[1] Wertheim, Ann. de Chim. et de Phys., *12*, 610, 1844. Edlund, Annal d. Phys., *129*, 15, 1866; *131*, 337, 1867. Streintz, Annal d. Phys., *150*, 368, 1873. Mebius, Oefvers. af k. Vet.-Akad. Forhandl., 681, 1887; Beibl., *12*, 678, 1888.

[2] PHYS. REV., O. S., Vol. 2, 279, 1895; Vol. 3, 433, 1896.

[3] Proc. Roy. Soc. Edin., Vol. 27, 343, 1907; Vol. 28, 652, 1907; Vol. 31, 186, 1910.

the value at 125° C. being about the same as at 20° C. Employing different loads he finds that the maximum is less with the heavier loads amounting to 11.9 per cent. for 18.3 kg. per sq. mm. and only 1.4 per cent. for 32.9 kg. per sq. mm. With steel wire Walker obtains similar results except that at higher temperatures the modulus is a little less than at room temperature and the magnitude of the change in the modulus is smaller. With a load of 23.3 kg. per sq. mm. the maximum value occurs at about 60° C. and is 1.9 per cent. greater than the value at 15° C. For 42.4 kg. per sq. mm. the maximum is at about 35° C. and amounts to 0.3 per cent. The load which I have employed is only 8.2 kg. per sq. mm. It would seem as if some trace of Walker's maximum ought to have appeared, but in my results there has been no indication of any such effect.

Walker[1] also studied the effect of variation of load while keeping the current constant at several different values. For some reason the results are now interpreted in terms of field intensity produced in the wire although formerly the effect of the current was regarded as one of temperature. The fields employed varied from 0.7 to 31.9 gausses for iron and from 0.65 to 33.7 gausses for steel. The loads were 14.6 to 36.5 kg. per sq. mm. and 16.9 to 46.7 kg. per sq. mm. respectively. In each case maximum values of the modulus appeared with intermediate values of both load and field. In the case of iron the maximum variation in the modulus for a given field was 11 per cent., the field being 9.1 gausses and the load 18.3 kg. per sq. mm. The maximum variation for steel was 2.4 per cent. and occurred with a field of 17.4 gausses and a load of 29.7 kg. per sq. mm. As these effects were interpreted as results of magnetic field intensity it is worthy of remark that exactly the same sort of variations were found with the non-magnetic metals copper and platinum.

In my own work the average field intensity is 3.25 times the current in amperes. It varied therefore from 0 to 29 gausses and since the external heating was sometimes used in conjunction it was not always the same for the same temperature. In no instance have I been able to detect any effect peculiar to the current or its accompanying magnetic field and any variation in the modulus amounting to more than one per cent. would have been observed.

Concerning the effect of magnetization upon Young's modulus a great deal of work has been carried on. The more important results have been those of Honda and Terada,[2] Honda, Shimizu, and Kusakabe,[3] Rensing,[4]

[1] Proc. Roy. Soc. Edin., Vol. 31, 186, 1910.

[2] Phil. Mag., Vol. 13, 36, 1907.

[3] Phil. Mag., Vol. 4, 459, 1902.

[4] Annal. d. Phys., *14*, 363, 1904.

Stevens and Dorsey,[1] Stevens,[2] Brackett[3] and Bock.[4] An effect has been observed but in every case it was small, amounting to less than one half per cent. As far as these results, which are for longitudinal and not circular magnetization, and my own can be compared with those of Walker there is flat contradiction. In the near future I hope to have more data as a basis for comparison. The differences may of course be due entirely to an inherent difference in the samples of wire.

The results of the earlier investigations of the temperature coefficient of Young's modulus of iron and steel wires were over rather limited temperature ranges and were subject to considerable error. Wertheim[6] found for iron a maximum in the neighborhood of 100° C. followed by a rapid decrease up to 200° C. A similar maximum appeared in English steel but not in cast steel. Kupfer[6] employing a method of bending rods found for several metals including iron and steel a decrease of elasticity with increase of temperature. More recently Gray, Blyth, and Dunlop[7] have worked with mild steel and Shakespeare[8] with a "silver" steel wire at room temperature and at or about 100° C. and found a decrease in the modulus per 100° C. of 2.47 and 3.8 per cent. respectively [1.5]. For iron wire the coefficients are 1.6 and 1.8 per cent. respectively while Katzenelsohn[9] reports 2.33 per cent. The bracketed figures here and following are results taken from my own work for corresponding temperatures. The work of Miss Noyes[10] was not sufficiently accurate to have detected other than a linear relation had it existed. She finds for four samples of piano wire with moduli of about 20.3 an average decrease of the modulus of 4.6 per cent. per 100° C.

On the other hand Pisati[11] finds for both iron and steel a decrease of the modulus at an increasing rate for a temperature range extending to 300° C. His value of the modulus for steel is 18.47. Heating from 25° C. to 300° C. produces a decrease of 6.3 per cent. [19.3, 6.7]. For iron the modulus was 21.43, the decrease, 12 per cent. Walker[12] found the modulus of a piece of soft iron wire to be 18.22 at 17.5° C. With ordinary heating up to 129° C. there was a uniform decrease amounting to 3.6 per cent. The

[1] PHYS. REV., O. S., Vol. 9, 116, 1900.
[2] PHYS. REV., O. S., Vol. 11, 95, 1900.
[3] PHYS. REV., O. S., Vol. 5, 257, 1897.
[4] Annal. d. Phys., *54*, 442, 1895.
[5] Ann. de chim. et de Phys., *12*, 385, 1844; *15*, 114, 1845.
[6] History of Elasticity, Todhunter and Pearson, Vol. II, p. 519.
[7] Proc. Roy. Soc., Vol. 67, 180, 1900.
[8] Phil. Mag., Vol. 47, 539, 1899.
[9] Diss. Berlin, 1887.
[10] *Loc. cit.*
[11] Nuovo Cimento, *4*, 152, 1878.
[12] Proc. Roy. Soc. Edin., Vol. 28, 652, 1907.

modulus of a steel wire was 21.6 at 15° C. It showed a decrease of 2.5 per cent. at 129° C. [19.3, 2.1].

The results of Pisati,[1] Gray, Blyth, and Dunlop,[2] Kohlrausch and Loomis,[3] and Slotte[4] upon the torsion modulus of iron and steel are of interest showing as they do a decrease of the modulus with increase of temperature, the decrease in nearly every case becoming more rapid at the higher temperatures.

Discussion of Errors.

At the lower temperatures the most important source of error is the measurement of the modulus. For temperatures below 350° C. the influence of the temperature upon the modulus is so small that errors in temperature are negligible in comparison. Above 350° C. the temperature effect becomes greater and greater and the errors in the temperature are the more important.

Even with the measurement of the stretch made with micrometer slides accurate to 0.001 mm. it is impossible to be certain of the value of the modulus from any single determination below 350° C. to a greater accuracy than one per cent. In some cases the results vary as much as two per cent. At 350° C. a change in the temperature of 20° C. would be necessary to produce a change of one per cent. in the modulus. At this temperature the measurement of the average temperature is accurate to about 10° C. which is entirely sufficient for the purposes of this investigation.

Above 350° C. the error in the modulus becomes greater amounting to three or four per cent. at 475° C. Over this range the rate of change of the modulus with temperature is so rapid that the errors in the modulus are now negligible in comparison with the temperature error which is perhaps as great as 20° C. at 475° C.

The errors in the modulus are errors of observation and in the plotting of the curves tend to cancel each other. The change of length can be observed to an accuracy corresponding to a temperature difference of one eighth of a degree. The temperature error is therefore due entirely to the difficulty of determining the relation between change of length and temperature, on account of uncertainty as to whether the thermo-couples give the true temperature of the wire. It is probable that this error is not more than 5° C. at 150° C., 10° C. at 350° C., and 20° C. at 475° C. and I am of the opinion that it is considerably less. If we were to con-

[1] *Loc. cit.*

[2] *Loc. cit.*

[3] Annal. d. Phys., *141*, 481, 1871.

[4] Acta. Soc. Scien. Fennicae, *35*, 1908.

sider the curves as moved, first, with a motion up and down a distance corresponding to one per cent. of the modulus and, second, with a motion to the right and left corresponding to twenty degrees variation in temperature, the true position of the curve would fall well within the area covered.

As explained in a previous section of this paper there is a variation of temperature along the wire amounting to 40° C. at 350° C. Consequently at any given average temperature the value of the modulus is the average of the moduli of elements of length some of which are at temperatures lower and some at temperatures higher than the average. In the case of current heating the variation along the wire is less but a variation in the cross section is introduced. It is assumed that the change of length averages the variation in temperature of the different cylindrical layers as well as the variation along the length. It should be noted that the value of the modulus is a similar average of the moduli of the different layers as well as the different elements of length. Except for the fact that sudden changes in the modulus, or in the slope of the curve, peculiar to some definite temperature would be concealed by this averaging these factors are negligible in comparison with the errors already discussed.

Attention has been called to the effect of magnetization on the modulus and mention is now made of magnetostriction,[1] the cooling of the wire on application of the weight,[2] and the apparent increase in length of the wire accompanying the straightening of the catenary only to call attention to the extreme smallness of these effects and the fact that they may be entirely neglected in this investigation.

SUMMARY.

The results of the tests that have been made upon this sample of mild steel wire may be summarized as follows:

1. The sample showed very erratic changes in elasticity when first heated.

2. By continued heating and stretching it was brought to a cyclic condition, or steady elastic state, in which Young's modulus becomes a function of temperature. This was secured first for a temperature range of 20° C. to 300° C., and later for a range extending to 475° C.

3. Continued heating and stretching gradually increased the modulus, the effect being probably caused largely by the stretching.

4. Except for the small gradual increase above mentioned, the modulus

[1] Honda and Terada, *loc. cit.* Honda, Shimizu, and Kusakabe, *loc. cit.* Dorsey, PHYS. REV., O. S., Vol. 30, 698, 1910. Brackett, PHYS. REV., O. S., Vol. 5, 257, 1897. Rhoads, Phil. Mag., Vol. 2, 463, 1901, and others.

[2] Joule, Proc. Roy. Soc., Vol. 8, 355, 1857; Phil. Trans., Vol. 149, 91, 1859; Scientific Papers, Vol. I, pp. 405, 413.

of the wire was independent of history, the thermal route by which any temperature was reached having no apparent influence upon the value of the modulus.

5. Heating by an electric current has no effect other than that caused by the accompanying temperature. This is in direct contradiction to the work of Walker. The very small changes in the modulus caused by magnetization reported by other investigators would not have been detected by this apparatus.

6. The Young's modulus of the wire decreased with increase of temperature at an increasing rate. The modulus decreased slowly and almost uniformly up to a temperature of about 300° C. Then the rate of decrease became more and more rapid, the plotted curve becoming very steep at 475° C. The following table is compiled from the various results.

TABLE II.

Change of Young's Modulus of a Mild Steel Wire with Increase of Temperature.

Temperature.	Modulus $\times 10^{-11}$ Dynes per Cm.^{2}	$\frac{dE \times 10^{-11}}{dT}$	Total Decrease, Per Cent. of E at 20° C.	Temperature.	Modulus $\times 10^{-11}$ Dynes per Cm.^{2}	$\frac{dE \times 10^{-11}}{dT}$	Total Decrease, Per Cent. of E at 20° C.
20° C.	19.3	.0035	0.0	300° C.	18.0	.0074	6.7
50	19.2	.0036	0.5	350	17.5	.0106	9.3
100	19.0	.0038	1.5	400	16.8	.0205	11.9
150	18.8	.0041	2.6	425	16.1	.0310	16.5
200	18.6	.0047	3.6	450	15.1	.0470	21.7
250	18.3	.0058	5.2	475	13.8	.0860	28.5

7. The values of the modulus are accurate to one per cent. for temperatures between 20° C. and 350° C. At 475° C. the error may amount to three or four per cent. Below 350° C. the temperature error is negligible in comparison to the error in the modulus. At 350° C. it may amount to 10° C. At higher temperatures the error is greater and of more importance on account of the more rapid decrease of the modulus. At 475° C. it is possible that the error may be as much as 20° C.

8. The above results while applying to but one sample of wire, when considered in the light of other investigations, appear to be characteristic and I should expect to find very similar effects with other samples of iron and steel.

In conclusion I wish to acknowledge indebtedness to the staff of the physical laboratory of the State University of Iowa for their interest in the work and especially to Professor G. W. Stewart for suggesting the problem.

PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA,
JULY, 1914.

THERMAL ELECTROMOTIVE FORCES OF IRON OXIDE AND COPPER OXIDE.

BY S. LEROY BROWN AND L. O. SHUDDEMAGEN.

THIS work suggested itself when it was noticed that a considerable electromotive force is generated when a cold wire is brought in contact with a similar or dissimilar hot wire. If two iron wires are fastened to the terminals of a galvanometer, one wire heated in a flame and the heated portion is touched with the cool wire, the electromotive force generated is many times sufficient to throw the galvanometer deflection off the scale. If two similar wires are brought together as described above and left in the flame, the electromotive force will reduce to zero or nearly zero; and, if two dissimilar wires are brought in contact and left in the flame, the thermal electromotive force will reduce to the value that is characteristic of the two metals with the hot junction at the temperature of the flame.

These large electromotive forces which are generated when one hot and one cold metal are brought in contact were found to be due to the oxides which formed on the heated metal, and experiments were planned to investigate the thermal electromotive forces at the junctions of oxide and metals. A preliminary report of this work and some values for the thermal electromotive forces of a copper-copper oxide couple were given at the Atlanta meeting of the Physical Society.[1]

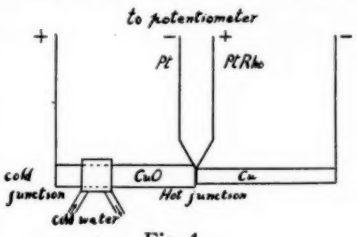

Fig. 1.

The oxides used in these experiments were of solid form and were prepared either by complete oxidation of metallic wires or by melting the oxide and molding into a solid rod. Solid rods of large cross-section were obtained by melting the powdered or finely divided oxides in porcelain tubes which were placed in a tubular electric furnace. In this manner, solid rods of magnetite (Fe_3O_4) and cuprous oxide (Cu_2O), which were from 5 to 15 centimeters long and nearly a centimeter in diameter, were prepared from the molten oxides. The resistances of

[1] Abstract, PHYS. REV., p. 239, March, 1914.

the oxides are enormous at lower temperatures, and therefore the large rods made possible more accurate measurements of the thermal electromotive forces in the case when an oxide formed one junction of a couple, since the large cross-section diminished the resistance.

The three oxides which were used as thermocouple elements were cupric oxide (CuO), cuprous oxide (Cu_2O), and magnetite (Fe_3O_4). The cupric oxide elements were made from completely oxidized no. 12 copper wires. The cuprous oxide elements were made by melting cupric oxide and quickly cooling from the molten state to a solid as it is molded in a porcelain tube. The high temperature required to melt cupric oxide (CuO) reduces it to cuprous oxide (Cu_2O) and, if quickly cooled to a temperature below 800° C., solid cuprous oxide is obtained. If this solid is

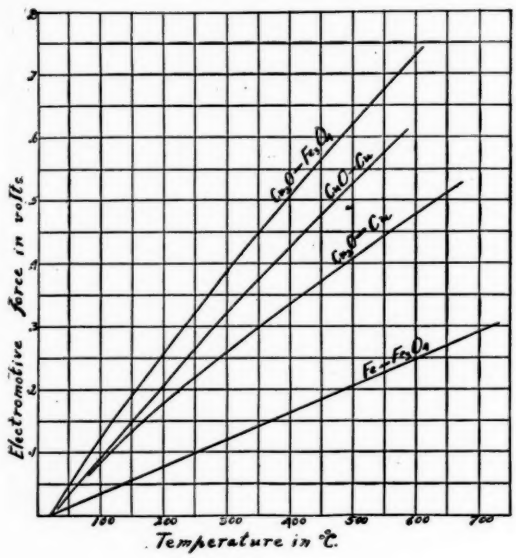

Fig. 2.

Thermal Electromotive Force Curves.

heated to about 800° C. it will decompose into free copper and cupric oxide. The magnetite elements were obtained by melting iron oxide and molding in porcelain tubes. The temperature to melt the iron oxide (Fe_2O_3) reduces it to magnetite (Fe_3O_4) and the solid formed from the molten state is solid magnetite.[1]

The thermal electromotive forces of the oxides were measured with a

[1] The authors are indebted to Mr. D. J. Brown, of the School of Chemistry, University of Texas, for analyses of these oxide elements which were found to be of the chemical composition as indicated in this paper except that the cuprous oxide element contained a small per cent. (1.5) of cupric oxide.

potentiometer, and the temperatures of the hot junction were measured with a standardized platinum-platinum rhodium thermocouple while the cold junction was maintained at room temperature. The junction of a metal and an oxide or of two oxides was made as shown in Fig. 1, the junction of the standard thermocouple being at the junction of the couple which was being investigated. A cooler through which water circulated maintained the cooler end of the oxide element at room temperature, while the hot junction was heated by means of a flame or an electric heating coil. The electromotive forces of the junction which was being examined were recorded only when the standard thermocouple indicated that the temperature of the junction was remaining approximately constant.

The following data and curves show the thermal electromotive forces

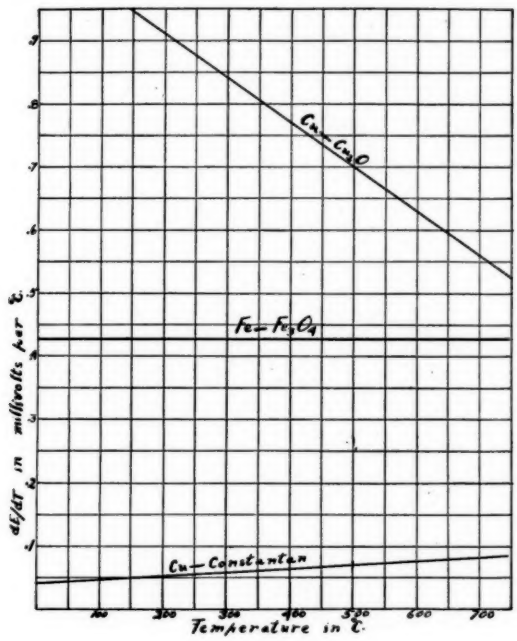

Fig. 3.

Thermo Electric Power Diagrams.

for copper-cupric oxide, copper-cuprous oxide, iron-magnetite, iron-cuprous oxide, copper-magnetite and cuprous oxide-magnetite thermocouples with temperatures of the hot junction ranging as high as 750° C. The data shows no appreciable difference, between the copper-cuprous oxide and iron-cuprous oxide couples, or between iron-magnetite and copper-magnetite couples. The electromotives forces as determined for

the cuprous oxide-magnetite couple could not be accurately measured on account of the extremely high resistance of a junction of two oxides but the data obtained gives points which lie near the curve which is obtained by an addition of the two metal oxide curves.

The electromotive force variation with temperature of a copper-cuprous oxide couple can be approximately expressed by the parabolic relation,

$$e = 1.0375(t - 20) - .000375(t - 20)^2 \text{ millivolts}$$

when the cold junction is at 20° C., or the thermo-electric power of this couple is

$$de/dt = 1.0375 - .00075(t - 20) \text{ millivolts per degree C.}$$

The electromotive force curve for the iron-magnetite couple is very accurately represented by the linear relation,

$$e = .427(t - 20) \text{ millivolts,}$$

or its thermo-electric power is

$$de/dt = .427 \text{ millivolts per degree C.}$$

The thermo-electric power lines for these two couples and a copper-constantan couple (for comparison) are shown in Fig. 3.

After several reheatings of a junction which has a cupric oxide element, its electromotive force will diminish and its electromotive force curve will approach the curve that is obtained when the cupric oxide element is replaced by cuprous oxide. That is, the higher temperature partially reduces the cupric oxide to cuprous oxide. When cuprous oxide is one of the elements of a couple, the junction cannot be subjected to temperatures higher than about 800° C. without decomposition, and this decomposition is accompanied by a decided decrease of thermal electromotive force.

The thermal electromotive forces developed by the above described couples are to the authors' knowledge very much larger than have been noted by previous experimenters. Weiss and Koenigsberger[1] noted a large thermal electromotive force for a junction of a metal and magnetite ore but their experiment was not carried to temperatures higher than 100° C. Bàédeker[2] measured the thermal electromotives forces for several metallic sulphides and oxides but only through a very small temperature range. Since the data in this paper were taken, an article has been published by C. C. Bidwell[3] which describes a very extensive research on thermal electromotive forces of oxides and which includes cupric oxide

[1] Phys. Zeitschr., *10*, p. 956.

[2] Ann. der Phys., *22*, 4, p. 749.

[3] PHYS. REV., March, 1914.

and magnetite. The values found by the authors for these two oxides are very much larger than the values found by Bidwell. This may possibly be accounted for by a difference in the preparation of the elements and hence different physical states. As stated before, the authors resorted to chemical analyses to make sure of the chemical compositions of the molten products which were used as thermocouple elements.

The cold junction was maintained at room temperature or approximately 20° C. for all the following data.

$(Cu)_-$ – (Cu O)+[1]		$(Cu)_-$ – $(Cu_2 O)_+$		$(Fe)_-$ – $(Cu_2 O)_+$	
Hot Jc., °C.	E.M.F., Volts.	Hot Jc., °C.	E.M.F., Volts.	Hot Jc., °C.	E.M.F., Volts.
95	.090	95	.078	100	.085
132	.135	152	.130	322	.280
187	.192	168	.148	497	.410
217	.226	177	.158	538	.434
252	.267	192	.168	642	.503
305	.330	236	.209		
325	.345	297	.261		
351	.375	305	.265		
375	.398	348	.296		
395	.422	407	.345		
445	.473	466	.388		
503	.524	527	.427		
525	.552	595	.474		
548	.573	665	.518		
570	.591	710	.542		
$(Fe)_+$ – $(Fe_3 O_4)_-$		$(Cu)_+$ – $(Fe_3 O_4)_-$		$(Cu_2 O)_+$ – $(Fe_3 O_4)_-$	
90	.030	102	.035	92	.112
175	.067	113	.041	155	.200
265	.104	240	.097	210	.276
300	.120	315	.125	280	.345
362	.144	357	.145	312	.405
404	.163	423	.175	405	.515
468	.190	550	.225	492	.602
517	.211			613	.745
565	.231			651	.770
588	.240				
602	.246				
640	.278				
670	.288				
693	.300				
725					

PHYSICAL LABORATORIES,
THE UNIVERSITY OF TEXAS.

[1] Each parenthesis represents an element of the couple and the positive or negative subscripts represent the polarity.

THE TOTAL LUMINOUS EFFICIENCIES OF PRESENT-DAY ILLUMINANTS.

BY HERBERT E. IVES.

LIGHTING science has lagged behind other branches of engineering in the definiteness of its quantitative aspects and in exactness of terminology largely through the chaotic condition of the question of luminous efficiency.

While the efficiency of a motor or a transformer may be derived in the form of a definite fraction or percentage from the direct comparison of output to input, both measured in the same units, the efficiency of an illuminant has not been so expressible. The engineer, who measures input in watts, and luminous output in lumens, expresses efficiency in lumens per watt, a ratio of value in comparing one illuminant with another, but one whose unit is very far from being the ideal efficiency which is understood by 100 per cent. efficiency in any other connection. The so-called "luminous efficiencies" to be found in physical literature might with greater propriety be called the "visible fractions" of the radiated power. They are expressed in percentage values, but the unit is not the most efficient illuminant—it is the most efficient illuminant possessing the same visible spectrum as the one measured. It affords no exact measure of comparison of one illuminant against another.

The unravelling of this tangle is attained by so defining luminous flux that its dimensions are the same as power, and by determining the constant of proportionality between the present arbitrary luminous flux unit and the power unit. These two steps have been taken in the definition of luminous flux as "radiant power evaluated according to its capacity to produce the sensation of light," and in the determination of the ratio of the lumen to the watt, recently published in this journal.[1] With these steps taken it is a simple matter to arrive at the luminous efficiency of any illuminant, given its power input, its power output, and its luminous output. It is only necessary to transform the last quantity from lumens to the equivalent watts, to have all the quantities in the same units. Then we have,

$$\frac{\text{Luminous output}}{\text{power input}} = \text{total luminous efficiency};$$

[1] PHYS. REV., The Mechanical Equivalent of Light.

$$\frac{\text{Luminous output}}{\text{radiant power output}} = \text{radiant luminous efficiency.}$$

Radiant luminous efficiency may be determined, as indicated, by knowledge of the radiated power and the watt value of the lumen. It can however be found much more simply by the measurement of the ratio of light-evaluated to unevaluated power. Measurements of this quantity have been made in this way by Karrer and reported in this journal.[1]

For the determination of total efficiency, on the other hand, it is necessary to measure each quantity in question, since different instruments and methods are required for each. It is here that the recently determined value of the lumen in terms of the watt is indispensable, and it is with this quantity alone that the present paper deals.

The lumen has been found to be .00162 watt. The "efficiency" of any illuminant in lumens per watt can, by the use of this constant, be translated into *watts of luminous flux per watt of power input.*

This is a simple fraction, on a scale of efficiency in which the value of the most efficient possible light source is unity.

An illustration will make clear the derivation of the values for total luminous efficiency given in the table. The standard carbon incandescent lamp has an efficiency in the present practical units of 2.59 lumens per watt. Now $2.59 \times .00162 = .0042$, the ratio of luminous output to power input expressed in the same units, or the total luminous efficiency. The construction of a table of total luminous efficiencies thus involves no more arduous labor than the multiplication of the lumens per watt of the illuminants of interest by a constant, that constant being the watt value of the lumen. If the watt is adopted as the unit of luminous flux, as the writer has suggested, the ratio of output to input as measured is at once the efficiency. The superiority of the watt over a unit based merely on a certain combination of wick and wax should not require much discussion.

In the case where the power consumption is expressed in a unit other than the watt, a prelimination transformation to watts should be made, or the corresponding constant may be worked out. Thus gas illuminant efficiencies are commonly expressed in "lumens per British thermal unit per hour." This may be reduced to lumens per watt by dividing by .293, or it may be reduced at once to total efficiency by multiplication by .00162/.293 or .00553.

The appended table of total luminous efficiencies has been prepared from data collected from a number of sources. A few figures are calculated from the very full table in Liebenthal's Praktische Photometrie where

[1] PHYS. REV., March 1915, p. 189.

Illuminant, Commercial Description.	Commercial Rating.	Efficiency in Present Units (Lumens per Watt).	Ratio Watts of Luminous Flux / Watts Input or Total Efficiency on Correct Scale.
Carbon incandescent lamp. Oval anchored (treated) filament.	4-watts per mean hor. C.P.	2.6	.0042
Tungsten incandescent lamp. Vacuum type.	1.25 watts per hor. C.P.	8	.013
Mazda, Type C	600 C.P.-20 amp. .5 w.p.c. Series type C.	19.6	.032
	500 watt, multiple, .7 w.p.c. Type C.	15	.024
Carbon Arc. Open arc.	9.6 ampere; clear globe	11.8	.019
Enclosed arc. Light opal inner; clear outer and street reflector.	6.6 ampere, D.C.	5.9	.0096
Series enclosed carbon arc; light opal inner; clear outer; street reflector	7.5 ampere, A.C.	5.6	.0091
Magnetite arc. Series luminous arc lamp; ornamental type; clear globe; standard electrodes.	6.6 ampere, D.C.	21.6	.035
Enclosed white flame carbon arc	10 ampere, A.C.	26.7	.043
	6.5 ampere, D.C.	35.5	.058
Enclosed yellow flame carbon arc	10 ampere, A.C.	31.4	.051
	6.5 ampere, D.C.	34.2	.055
Open arc, white flame, inclined trim	10 ampere, A.C.	29	.047
	10 ampere, D.C.	27.7	.045
Open arc, yellow flame, inclined trim	10 ampere, A.C.	41.5	.067
	10 ampere, D.C.	44.7	.072
Moore Nitrogen Vacuum Tube	220-volt, 60-cycle, tube length 113.17 feet	5.21	.0085

Illuminant, Commercial Description.	Commercial Rating.	Efficiency in Present Units (Lumens per Watt).	Ratio Watts of Luminous Flux / Watts Input or Total Efficiency on Correct Scale.
Quartz Mercury arc[1]	174–197 volt; 4.2 ampere	42	.068
Glass Mercury arc[1]	40–70 volt; 3.5 ampere	23	.037
Nernst lamp[1]		4.8	.0077
Acetylene[1]	1.0 liters per hour consumption	.67	.0011
Petroleum lamp.[1]		.26	.0004
Incandescent gas lamp ('ow pressure)	.350 lumens per B.t.u. per hr.	1.2	.0019
Incandescent gas lamp (high pressure)	.578 lumens per B.t.u. per hr.	2.0	.0032
Open flame gas burner	Bray 6' high pressure	.22	.00036

[1] = figures from Liebenthal's Praktische Photometrie.

they are given in Hefner lumens per watt. The figures for the more recent illuminants have been collected from authoritative sources to whom acknowledgment is made below.

A difficulty in the collection of such data lies in the common practice of publishing efficiencies in terms of horizontal or hemispherical watts per candle, instead of mean spherical. The latter is of course the only value of use in calculating total efficiencies.

It is at once obvious from these figures that light is at present only a by-product. The highest efficiencies tabulated are those of the mercury arc in quartz and the yellow flame arcs. In both cases, however, the figures are misleading, because the overall efficiency is much reduced by the steadying resistances which are indispensable for the practical operation of these light sources.

The highest present efficiencies of light production do not exceed probably 5 per cent. of what should be possible.

Perfect efficiency on this scale of course means monochromatic green light. But even if the most efficient continuous spectrum *white light* is taken as the goal, this present 5 per cent. is increased only to 5/.40 or 12.5 per cent., the most efficient white light being about 40 per cent. efficient.[1]

It is of interest to compare these total efficiencies with the corresponding radiant efficiencies as determined by Karrer. The ratio:

$$\frac{\text{total efficiency}}{\text{radiant efficiency}} = \frac{L/P}{L/R} = \frac{R}{P}$$

(L = luminous flux, P = power input, R = radiant power) gives the *radiation efficiency* or fraction of the applied power which is transformed into radiation.

Now in the case of the carbon vacuum incandescent lamp the radiation efficiency = .0042/.0045 or over 90 per cent., while in the case of the incandescent gas burner this ratio is .0019/.012 = .16; in other words five-sixths of the applied power is lost as convection and conduction.

The writer takes pleasure in acknowledging his indebtedness to Mr. S. L. E. Rose, Mr. T. H. Amrine and Mr. R. B. Chillas for data on the electric illuminants.

PHYSICAL LABORATORY,
THE UNITED GAS IMPROVEMENT COMPANY,
PHILADELPHIA, PA.

[1] Ives, Electrical World, June 15, 1911.

THE NATURE OF ELECTRIC CONDUCTION AS REQUIRED TO EXPLAIN THE RECOVERY OF RESISTANCE OF METALLIC SELENIUM FOLLOWING ILLUMINATION.

BY F. C. BROWN.

DIFFERENT theories have been proposed to explain the transportation of electricity in solids, but metallic conductors generally have not offered satisfactory evidence for a final decision between the theories. The illuminating experiments on thermionics by Richardson and his students and also the consistent agreement of theory and experiment involving the ratio of the electrical to the thermal conductivity of metals have made various modifications of the dynamical equilibrium theory very popular. The seemingly most contradictory evidence to this theory is the low value of the specific heat for all the metals. However, Sir J. J. Thomson[1] has shown that the calculated and experimental ratios of the electrical to the thermal conductivity may agree equally well by a theory that presumes the electrons to be tied up with the atom in the form of a doublet. In this case electric conduction would be merely the transportation of electron from doublet to doublet much in the same way as the Grotthus chains in the old theory of electrolysis.

I shall in this paper present information which leads away from the first mentioned view above and which forms the basis for a theory bearing more or less resemblance to the above mentioned second theory of Thomson. For the reason that the conducting power of metallic selenium crystals may be varied by so many physical conditions, we have the obvious opportunity of making very definite choice as to what form of the electron theory is satisfactory. Having obtained a consistent theory for selenium, we can then decide if reasonable modifications of the theory will explain conduction in the other elements, where there are less favorable means of attack.

The investigations described in this and succeeding papers will be somewhat along the line of attack made by J. W. Nicholson.[2] An effort will be made to choose experiments that enable decision to be made with

[1] Book on the Corpuscular Theory of Matter, 1907.

[2] PHYS. REV., N. S., Vol. 3, p. 1, 1914. See also article by Merritt, PHYS. REV., 25, p. 505, 1907, which involves some of the elements of the ideas in this paper.

a minimum number of assumptions. The author is not aware of any direct or indirect measurements having been made which consider any particular value for the rate of recombination of electrons with their positive residues, except in the conduction of electricity through a gas under the influence of an ionizing agent. The subject will be opened by a consideration of the rate of recombination of the electrons and some of the conditions that influence this rate.

THEORETICAL CONSIDERATIONS.

It will be assumed that the specific conductivity varies as the number of electrons taking part in the conduction at any instant. The electrons do not exist free in the sense of the kinetic theory of gases. Under illumination they are rendered unstable or free but on the average they recombine with the atomic structures very rapidly. Experiment shows that following intense illumination thirty per cent. of the extra electrons return to their fixed positions in .02 second. A second assumption that will be made is that the recombination of the freed electrons will take place according to the same law governing the recombination of ions in gases. Then the rate of recombination of electrons will be expressed as,

$$\frac{dN}{dt} = -\alpha N^2, \tag{1}$$

where N is the average number of electrons in the free state at any instant and α is the coefficient of recombination. However, this equation holds only for a uniform distribution of the electrons. Such a distribution would exist when the selenium reaches the equilibrium condition in the light, or for the first small interval of time, Δt, after the illumination is shut off. The theory will presuppose that the coefficient of recombination is not altered by the condition of light or dark, and the experiments will verify this presumption.

Since the conductivity is proportional to the number of free electrons, we may write,

$$i = k_1 \cdot N \tag{2}$$

from which it follows that

$$\frac{di}{dt} = -\frac{\alpha i^2}{k_1}, \tag{3}$$

or

$$\frac{di}{dt} = -\alpha' i^2,$$

where α' is merely a new constant.

When the selenium is in equilibrium in the light the rate of recombination of the electrons is exactly equal to the rate of production of

electrons by the light in addition to the natural production in the dark. This may be represented as

$$\frac{dN}{dt} = M + q,$$

or

$$\frac{di}{dt} = k_1(M + q), \tag{4}$$

where M is the former rate and q is the latter or dark rate. Combining equations (3) and (4) we obtain, for the equilibrium value of the current,

$$i_e = k_1\sqrt{\frac{M+q}{\alpha}}. \tag{5}$$

Now we could check the theory by the application of observed data to satisfy equation (5), but the rate of production of electrons by light, M, is dependent upon the light intensity and therefore it will be more convenient to test the adequacy of the equation in the next succeeding paper, together with the law governing the rate of production with varying light intensities. It will be the purpose of this paper to verify the fundamental relation of rate of recombination to the number of free electrons, as expressed in equations (1) and (3). It was found that equation (3) could be verified when expressed in the approximate form

$$\frac{\Delta i}{\Delta t} = -\alpha' i^2, \tag{3}$$

when Δt was kept a very small interval of time and constant. Ordinarilly we should expect to check this equation by the application of its integrated form,

$$\left(\frac{1}{i} - \frac{1}{i_0} = \alpha t\right)$$

to a complete recovery curve extending over a considerable length of time. However, I have found that this can not be carried out satisfactorily because as soon as a large percentage of the electrons have recombined, a non-uniform distribution of the electrons and uncombined atoms exists, such that the coefficient of recombination is diminished. But it is not essential to the argument of this paper to either prove or disprove this statement. A slow diffusion of the electrons, and changing crystalline structure, no doubt are complexities to be taken into account in explaining a complete recovery curve.

That equation (3) is tenable, together with the underlying assumptions mentioned, may be ascertained from some observations taken with masses of crystals some years back. In my paper on the " Recovery of the Giltay Selenium Cell and the Nature of Light Action in Selenium "[1] on p. 415

[1] PHYS. REV., Vol. 33, p. 403, 1911.

is just such data as desired. The conducting component, B, has the same significance as i or N in this paper. The recovery during the mean interval of .05 second was measured after the selenium had begun to recover from illumination of varying intensities. The varying intensity produced the varying conductivity noted in the following table.

Conductivity in Dark. i_0	Conductivity in Light. i	Change of Conductivity, Ohms^{-1}. $\Delta i = k \cdot N$	$\frac{\Delta i}{i}$	$\frac{\Delta i}{i^2}$	Coefficient of Recombination. $\alpha' = \frac{\Delta i}{i^2 t}$
1.47×10^{-6}	6.29×10^{-6}	0.016×10^{-5}	2.5×10^{-2}	4.0×10^{3}	80×10^{3}
	13.5 × "	0.11 × "	8.2 × "	5.9 × "	118 × "
	60.2 × "	2.79 × "	46.5 × "	7.6 × "	152 × "
	35.4 × "	1.05 × "	29.6 × "	7.9 × "	158 × "
	50.8 × "	2.04 × "	40.2 × "	7.4 × "	159 × "
	16.1 × "	0.18 × "	11.2 × "	6.9 × "	138 × "

It may be observed, where the change of conductivity varies over the extreme range of from .016 to 2.79 (*i. e.*, by a factor of 174) that $\Delta i/i^2$ is approximately a constant. The values of α' as recorded in the last column are slightly in error because no allowance is made for the liberation of electrons taking place in the dark simultaneously with their recombination. If no new postulates are involved this correction should be of magnitude, $(i_0^2 \cdot \alpha' \cdot \Delta t)$, when added to Δi for the calculation of α'. Since this correction involves an error of less than ten per cent. in any value above, we will not complicate the argument of this paper by the application of this correction or considerations of the adequacy of the correction. Since the range of application of the data is so great, we may regard the constancy of the coefficient of recombination as satisfactory evidence that the electrons recombine with the atomic structures in accordance with the conception involved in equation (1), when the conditions are as specified. Since writing this paper I have also verified this fundamental conception by experiments on the recovery of single isolated crystals of selenium. This agreement of behavior of crystals and crystal aggregates is quite consistent with the other unique properties existing in the crystals, such as the likeness of the wave-length,—sensibility curves.[1]

It may be noted that a constant coefficient of recombination involves the idea that the number of electrons freed in dark recombine at a more rapid rate, when the selenium is illuminated or just following illumination. This follows because there are more positive residues and consequently more chances for recombination.

It should also be noted that Plimpton[2] has observed that ions in gases

[1] PHYS. REV., N. S., Vol. 4, p. 507, 1914; Vol. 5, p. 65, 1915.

[2] Am. Journ. of Sc., Vol. 35, p. 39, 1913.

also recombine according to the same law involved in equation (1), only in case there is a uniform distribution of ions. However, this agreement of the law of recombination of electrons in selenium with the recombination of ions in gases does not further lead us to suspect that the electric current may be transported by the same method in both selenium and in gases. The current in selenium with a given low potential is infinitely larger than any ionization current in gases, except in spark discharge. Further differences and likenesses of the method of transportation of the current will be brought out in later developments of the theory.

THE INADEQUACY OF OHM'S LAW.

A fundamental property in metallic selenium exists in the inadequacy of Ohm's Law to explain the variation of the current with the applied voltage. In all cases the current increases more rapidly than the proportional increase of the voltage. It is therefore pertinent to inquire what conditions are responsible for this unique property. According to the theory involved in equation (5) an increased potential can vary the specific conductivity only in two ways, by varying the rate of production of the electrons or by varying the rate of recombination of the electrons.

We will suppose that the increase of current necessary to satisfy Ohm's Law, when the voltage is increased, arises from increased velocity of drift of the electrons, and that the slight excess current arises from additional electrons in the conducting state. This increased number might come either from a magnified rate of production or from a diminished rate of recombination.

The increased rate of production might be expected because of bombardment of semi-fixed electrons by the faster moving ones or the greater electric intensity might be considered as lowering the degree of stability of all the electrons of a certain class in the atomic structure. Consistent with either of these views, it would be reasonable to expect a diminished rate of recombination as the voltage is increased. An increased velocity of drift would lessen somewhat the chance of an atom to capture an electron and also a lower stability of the atom would indicate a smaller attractive force for the electron.

A measurement of the recovery during a short interval following the extinction of the illumination should determine whether the coefficient of recombination varies with the applied potentials in such a manner as to explain the inadequacy of Ohm's Law.

The change of conductivity during short periods of recovery was measured by the Wheatstone's bridge and pendulum method.[1] The light

[1] PHYS. REV., Vol. 33, p. 54, 1911.

was cut off the selenium at the desired time by an aluminum shutter attached to the timing pendulum. A single lamellar crystal of metallic selenium of the fifth system was used for this investigation. The intensity of illumination from which the crystal recovered was kept constant. Also the pressure on the crystal was fixed at such a value that the resistance was 1,349,000 ohms with 1.45 volts. The change of conductivity was measured for the first 0.05 second interval of recovery, both when 1.45 volts was the difference of potential across the crystal and when there was 20 volts.

The change of conductivity during recovery of 0.05 seconds is shown in the following table. For convenience 0.05 second is here considered as the unit of time.

	With 20 Volts.	With 1.45 Volts.
Resistance in dark	1,192,000	1,349,000
Resistance in unvarying light	356,000	392,000
Conductivity in light	$i = 28.1 \times 10^{-7}$	$i = 25.5 \times 10^{-7}$
Recovery after 0.05 second	$i = 15.65 \times 10^{-7}$	$i = 14.1 \times 10^{-7}$
Change of conductivity	$\Delta i = 12.5 \times 10^{-7}$	11.4×10^{-7}
$\alpha' = \frac{\Delta i}{\Delta t \cdot i^2}$	1.58×10^5	1.75×10^5
$\frac{\alpha'}{i} = \frac{\Delta i}{i} = \frac{\Delta N}{N}$	0.447	0.447

It may be observed that the coefficient of recombination is not constant. In fact a brief consideration of the data reveals that this coefficient varies directly as the specific resistance of the crystal, when the variation of the specific resistance accrues from an altered potential difference between the crystal electrodes. This conclusion is verified by the constant ratio of α'/i, as recorded in the last row above.

If the constant, α', were the sole quantity that changed its value with varying potentials across the crystal, then we might expect in accordance with equation (5) that the equilibrium light sensitiveness of the crystal would vary inversely as the square root of α. However, the data for the same crystal that is given in the following table shows that the equilibrium light sensitiveness is almost proportional to the conductivity in the light. Since (α) varies inversely as the same conductivity in the light, and since the conductivity is influenced only by the square root of the recombination constant, it follows that the light sensitiveness should, according to equation (5), vary directly by some function of $M + q$, and further that this function should have the same value as the function relating (α) to the conductivity. This idea is a little beyond the province of this paper and will need to be verified further.

Potential across the crystal in volts	1.5	6.0	36	60
Conductivity in dark	5.9×10^{-7}	6.0×10^{-7}	6.85×10^{-7}	7.5×10^{-7}
Conductivity in light	20×10^{-7}	20.4×10^{-7}	23.3×10^{-7}	24×10^{-7}
Equilibrium light sensitiveness	14.1×10^{-7}	14.4×10^{-7}	16.5×10^{-7}	$16.5 - 10^{-7}$
$\frac{\text{Light sensitiveness}}{\text{Conductivity in light}}$	.705	.70	.70	.69

THE PRESSURE EFFECT.

The increase of the specific conductivity of selenium, by pressure, whether in isolated crystals or crystal aggregates is another unique principle that our electron theory should explain.[1] The specific conductivity may vary a hundred fold by increasing the pressure. According to the postulates in the earlier part of the paper, this increase of conductivity must arise either from an increase in the number of electrons capable of taking part in the conduction or in a decrease in the ratio of recombination of the electrons with the positive residues. From a consideration of the increase of the absolute light sensitiveness with increased pressure I have already concluded[2] that it would be unreasonable to expect the light-sensitiveness to increase in proportion to the conductivity in the dark, if the conductivity must vary alone with the number of electrons liberated.

Since there is no reason to expect any large changes of conductivity resulting from variations in the free path of the electron, it seemed very plausible that pressure might alter the rate of recombination of the electrons.

In the experimentation, the selenium crystal was placed between brass electrodes and the variable pressure desired was controlled by a screw adjustment. At each pressure the equilibrium conductivity was measured both with the crystal in the dark and with constant illumination. The recovery was measured during the first mean period of .02 second after the extinction of the illumination as elsewhere described. A constant difference of potential of 13 volts was kept between the crystal electrodes. The equilibrium conductivity in the light was attained in less than a second after illumination.

The following table shows the value of the coefficient of recombination for various pressures on the crystal such that the conductivity varied from 1.79×10^{-7} to 23.8×10^{-7} in the dark.

Since the pressure effect is of such large magnitude as noted, we may conclude (from the constant value of $\alpha' \cdot i$) with some certainty that the

[1] Brown and Stebbins, PHYS. REV., Vol. 26, p. 273, 1908; PHYS. REV., N. S., Vol. 4, p. 85, 1914.

[2] *Loc. cit.*, article above.

Pressure.	Conductivity in Dark Ohms^{-1}.	Conductivity in Light Ohms^{-1}.	Recovery in .02 Sec. Change of Conductivity. $i = K \cdot N$	$a' = \frac{\Delta i}{i^2 \cdot \Delta t}$	$a' \cdot i$
P_1	1.79×10^{-7}	5.18×10^{-7}	1.84×10^{-7}	3.5×10^{7}	17.9
P_2	$6.50 \times$ "	$15.4 \times$ "	$4.12 \times$ "	$1.35 \times$ "	17.1
P_3	$12.2 \times$ "	$30.3 \times$ "	$9.02 \times$ "	0.445	14.2
P_4	$18.9 \times$ "	$43.9 \times$ "	$14.36 \times$ "	0.300	15.0
P_5	$23.8 \times$ "	$55.5 \times$ "	$15.5 \times$ "	0.26	14.0

coefficient of recombination varies inversely as the initial conductivity in the light, that results from the pressure.

Now it may be observed in the same table of data that the light sensitiveness at the different pressures is almost proportional to the conductivity in the dark accompanying each pressure. If, in equation (5), the value of q were small compared with M, it would be necessary for M (the rate of production by a fixed illumination) to vary directly with the initial conductivity at any pressure in order that this increase of light sensitiveness might be proportional to the dark conductivity.

We have, therefore, proved that the coefficient of recombination varies inversely as the conductivity ensuing from the pressure, and the evidence just stated inclines very much toward the view that the rate of production by light varies directly as the same conductivity resulting from the pressure effect.

General Considerations.

The attempt has been made to build up a simple electron theory to correlate the most fundamental photo-electro-mechanical properties in metallic selenium. The experiments have been carefully selected to verify the basic conceptions with a minimum number of postulates, by avoiding all questions of absorption, reflection and time rate of change of conductivity.

The effort has been successful in achieving a simple consistency of results. It was first shown that the electrons do recombine very rapidly with what is supposed to be the atomic structures, and the recombination takes place according to the same law governing the recombination of ions in gases. But we can not conclude from this that the current is transported in the same way in selenium as an ionization current in gases.

The basis of the theory receives further support in that a common explanation accounts both for the variation from Ohm's law and for the large changes of conductivity accompanying pressure changes. In each case the coefficient of recombination of the electrons is found to vary inversely as the variable conductivity imposed by the pressure change or the difference of potential. And likewise, there is common evidence that the rate of production of conducting electrons by a fixed illumination is

directly proportional to the variable conductivity imposed by pressure or voltage.

The temporary liberation of electrons by light bears certain resemblance to the original suggestion of Pfund[1] in which he compared light-action in selenium to an internal photo-electrical effect. This idea also is consistent with the experiments of Dr. L. P. Sieg and the author[2] where we have found all isolated crystals of selenium to have a maximum sensibility in the ultra-violet region of the spectrum.

But the experiments indicate a distinctly new idea as involved in a coefficient of recombination of the electrons that varies with the physical conditions surrounding the crystal, and also a varying rate of production of electrons with a fixed light intensity. This varying rate of freeing of electrons is governed by the same law apparently as that governing the variation of the recombination constant, except that the two relations are in inverse direction.

The form of the electron theory as here presented offers a satisfactory explanation of the electro-dynamical, light-electrical and electrical relations recently published.[3] The action due to pressure is not transmitted beyond the region of stress. The pressure merely lowers the stability of the selenium such that a given light intensity may liberate a greater number of electrons where this stress exists and such that the electrons recombine less rapidly in the same region.

Consistent with this interpretation, the light action transmitted to a distance is increased if the pressure is applied to the portion of the crystal where the conduction takes place, but the transmitted effect is not increased by pressure applied only at the place of illumination. The transmitted light action is of the nature of a crystal disturbance, which lowers the stability of the electrons everywhere in the confines of the crystal.

Since the analysis has shown the voltage effect to be identical with the pressure effect so far as the rate of recombination of electrons or their liberation is concerned, it is to be expected that the voltage effect could not be transmitted throughout the crystal in the way that light action is transmitted. This, in fact, is the result found in the previous work.[4]

Naturally the theory suggests many other lines of investigation in order to obtain more detailed information as to the nature of electric conduction in selenium. Since we have already considered such a wide range of experiments and have obtained such satisfactory agreement, the theory is one of unusual promise.

[1] PHYS. REV., Vol. 28, p. 234, 1909.
[2] PHYS. REV., Vol. 4, p. 48, and p. 507, 1914.
[3] PHYS. REV., N. S., 1914.
[4] *Loc. cit.*

SOME EXPERIMENTS ON THE NATURE OF TRANSMITTED LIGHT-ACTION IN CRYSTALS OF METALLIC SELENIUM.

BY F. C. BROWN.

RECENTLY we showed[1] that light falling on one part of a crystal of selenium would produce a change of conductivity throughout the crystal. In the acicular crystals this effect was observed practically undiminished in amount as far as 10 mm. away from the point of illumination. This effect was denoted by the authors as a new property in matter. The work described in this paper consists essentially of two investigations designed to give information concerning the nature of this light-action. The first was an experiment to determine the velocity of transmission of the light effect along the crystal, and the second was a study of certain interrelated phenomena between the pressure effect[2] and the transmitted light action. The one showed the action to be transmitted much too rapidly for a temperature effect. The other definitely proved that the increase of conductivity at a distance could not arise from transmitted free electrons. Incidently, the results call forth a new view as to the nature of electrical conduction as exhibited in crystals of metallic selenium.

THE RATE OF TRANSMISSION OF LIGHT-ACTION ALONG THE CRYSTALS.

To obtain information as to the rate of transmission of this new effect the method used was to determine the resistance after short intervals of time following illumination at a distant point. A lamellar crystal of the fifth system, of size about 4 × .6 × .3 mm., with striations perpendicular to the length of the crystal was mounted with opposite ends between separate sets of electrodes as shown conventionally in Fig. 1. Under crossed nicols the crystal would show parallel extinction. A constant source of illumination was obtained by focussing a Nernst glower on the crystal.

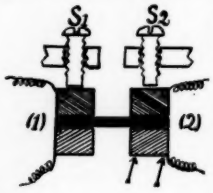

Fig. 1.

[1] Brown and Sieg, Phil. Mag., Ser. VI., Vol. 28, p. 497, 1914; Brown, PHYS. REV., N. S., Vol. IV., p. 85, 1914.

[2] For a description of this effect see paper by author in PHYS. REV., Ser. 2, Vol. 14, p. 85, 1914.

The procedure was to connect the resistance between electrodes at end (2) in one arm of a Wheatstone's bridge circuit. The resistance of this part of the crystal was measured in the dark and when it was illuminated, and then the same part was measured again when the opposite end (1) was in the dark and then in equilibrium under the same constant illumination as was previously on the conducting end. Next the above procedure was repeated several times, with the modification necessary to measure the change of resistance during the first 0.4 second of illumination. The object was to determine what part of the total change of resistance was transmitted two millimeters along the crystal in this short interval. Of course, even if the light falls directly on the part of the crystal whose resistance change is under determination all the effect does not take place at once.[1] Thus the opposite ends of the crystal were illuminated alternately in order to find the relative lag in the transmitted effect.

The method of measuring the change of resistance in these small intervals was that described by Brown and Clark.[2] A shutter was attached to a ballistic pendulum, which automatically put a galvanometer in circuit for a short interval at any desired time after the shutter moved out of the path of the beam of light directed on the crystal. Thus in Table I. the change of resistance was recorded as divisions throw of the galvanometer, which was afterward reduced to ohms.

In the first series of observations, where the conductivity of end (1) of the crystal was measured there is a rather wide variation of the readings, but this was brought about by a deliberate variation of the lighting arrangement, extra screens to cut off stray light, etc., being used. The purpose was to make observations under corresponding conditions when each end was illuminated.

The result of these experiments can be stated as follows:

Both the direct and the transmitted actions are very rapid, more than 50 per cent. of the equilibrium change taking place in 0.4 second. In searching for an explanation of the fact that the percentage change of conductivity in 0.4 second was quite different depending on which end of the crystal was tested, facts were discovered which indicate that the ratio of the area illuminated to the cross sectional area conducting is a factor in the rate of change in short intervals of time. Whatever may be the outcome of a study of this relation, it is not believed that the accompanying results will be at all vitiated. Second, that the total amount of the transmitted action is of the same order of magnitude as the direct action and yet distinctly less. Third, the difference between

[1] See PHYS. REV., Vol. 33, p. 403.

[2] PHYS. REV., Vol. 33, p. 53, 1911.

TABLE I.

Change of Resistance of Crystal at End (1).

	Illuminated at Electrode (2), Ohms.	Illuminated at (1), Ohms.
Resistance in dark	880,000	880,000
Resistance in equilibrium with light	450,000	370,000
Change of resistance at equilibrium	430,000	510,000
Change of resistance in 0.4 sec.	7.0	9.0
	7.5	9.0
	7.0	11.5
	9.0	12.0
	9.0	12.5
	8.0	12.0
	7.5	12.0
	9.0	15.0
	11.0	15.0
	11.0	18.0
Mean in div.	8.6	12.9
Mean ohms.	183,000	234,000
Ratio, $\frac{\text{change in 0.4 sec.}}{\text{equilibrium change}}$	.426	.459

Change of Resistance Measured at End (2).

	Arranged to Illuminate end (1).	To Illuminate (2).
Resistance in dark	510,000	510,000
Resistance in equilibrium in light	340,000	260,000
Change of resistance at equilibrium	170,000	250,000
Change of resistance in 0.4 sec	11.0	18.0
	10.5	17.5
	11.0	16.5
	11.0	16.5
	10.0	14.5
Mean in div.	10.7	16.6
Mean in ohms.	136,000	215,000
Ratio, $\frac{\text{change in 0.4 sec.}}{\text{equilibrium change}}$	.80	.86
Change of resistance in 0.2 sec.	10. div.	16.
	10.5	15.5
Mean in ohms.	133,000	201,000
Ratio, $\frac{\text{change of resistance in 0.2 sec.}}{\text{equilibrium change}}$	.78	.80
Change of resistance in 0.1 sec.	7.0 div.	13.5
	7.5	12.5
	7.5	12.5
Mean	7.3	12.8
In ohms.	95,000	162,000
Ratio, $\frac{\text{change in 0.1 sec.}}{\text{equilibrium change}}$	.56	.65

the fractional parts of the total change taking place in 0.4 second for the direct and the transmitted effects is very small. The proportional change in 0.2 second is also observed to be the same within the limits of accuracy of the measurement. Even for 0.1 second exposure there is almost as great a fraction of the effect transmitted to the opposite end of the crystal as at the illuminated end.

The conclusion is fairly safe that practically all of the transmitted action by light may travel a distance of 2 mm. in less than 0.1 second. How much faster than 2 centimeters per second it may travel, I was not prepared to determine. At any rate the effect travels so fast that we are warranted in saying that it can not be transmission of a temperature change along the crystal. This conclusion is quite in agreement with recent experiments by Sieg and Brown,[1] in which it was shown that for equal quantities of energy in different parts of the spectrum falling on the crystal, a maximum transmitted effect occured in the visible spectrum, not far from the position where the maximum occurred for direct action of the light. Likewise, if the transmission is too rapid to be a transmitted temperature disturbance, it must, according to the electron theory, be too rapid to be merely an equalization of electronic pressures throughout the crystal.

THE ACTION AT A DISTANCE IS PROPAGATED MECHANICALLY.

The fundamental fact is that light falls on a crystal of selenium at one spot and produces a change of conductivity at any other part of the crystal. It is inconceivable that the light itself could, on entering a crystal, diffuse almost without absorption to the most distant part of a crystal, and yet such may be the case. Therefore the nature of this transmitted effect was investigated along other lines. One view would suppose the light by virtue of its electromagnetic properties to be able to directly tear the electrons free from the atomic structure. In order that there might be almost undiminished action at a distance, either these electrons must disperse to all parts of the crystal structure or at the place where the light falls there must be an increased concentration of electrons which would quickly be felt throughout the crystal, the same as an increased quantity of gas in one part of a tank system would be felt everywhere in the enclosure. The velocity of such a disturbance would be largely a function of the elastic properties of the electrons in confined space. Another view is that the light acts upon a certain mechanism which produces automatically a certain instability throughout the crystal structure. This instability manifests itself by a greater electrical con-

[1] PHYS. REV., N. S., vol. 4, p. 507, 1914.

ductivity, which means either an increased number of free electrons or a greater instability of the fixed electrons. The first view involves the direct carrying over of the action without the aid of the crystal structure as such while the second view involves something analogous to an elastic medium propagation.

The merits of the above views were investigated largely with the use of the arrangement shown in Fig. 1. In my previous paper it was pointed out that the resistance of a crystal varies with the mechanical pressure under which it exists and also that the resistance varies with the potential differences producing the current. With this apparatus were studied the interaction of various agents, viz. light, pressure and electrical potentials, that alter the resistance of the crystal.

It was found, no matter how much the resistance might change at end (1) as a result of large differences of potential there, that the resistance at the opposite end (2) did not vary. Similarly pressure on end (1) of the crystal by the screw S_1 changed the resistance at (1) by a factor of ten but the resistance at the opposite end was thereby changed only by a zero or negligible amount. Thus we have the clear cut result that *light-action is transmitted along the crystal, but the pressure effects and the electrical potential effect*, as I have designated them, *are not transmitted.*

A most important part of the experiment was in the superposition of the pressure and the light effects. In this experiment only end (1) of the crystal was illuminated in all the observations. The conductivity was measured at both ends simultaneously, both when end (1) was in the dark and when it was illuminated. The observations are shown in Table II. The pressures were deduced from the conductivity values according to the relation found in an earlier paper.[1] The illumination was practically constant throughout. A brief study of the table will verify the following generalization: *the increase of pressure increases the light sensibility* (*i. e., the change of conductivity due to constant illumination*) *only when the pressure is applied to the part of the crystal where the conductivity is being measured.*

From the results stated we are warranted in making the following deductions: If electrical conduction in these crystals is due to *free electrons that exist in equilibrium according to the Maxwell-Boltzman law, it can not be possible that the mechanical pressure in increasing the conductivity increases the number of free electrons.* This follows because the pressure effect is not transmitted from one part of the crystal to another and because the light-sensitiveness with varying pressure remains constant everywhere except at the points where the pressure is applied. There might, of course,

[1] PHYS. REV., Ser. 2, Vol. 4, p. 85, 1914.

TABLE II.

Conductivity of Lamellar Crystal, $\times 10^7$.

	Between Electrodes at (1).	Between Electrodes at (2).
In dark.....	4.0, 4.0, 4.0	4.8, 4.5, 5.0
End (1) illuminated.	7,8, 8.0, 8.0	6.9, 7.4, 7.7
Increase of conductivity.....	3.8, 4.0, 4.0 mean 3.9 div.	2.1, 2.9, 2.7 mean 2.6 div.
Pressure on (1) 3, kgm./cm². on (2) 2 kgm.		
Pressure increased by S_1.		
In dark.....	8.0, 8.8, 8.8	5.2, 5.3, 5.3
End (1) illuminated.	16.0, 16.6, 16.4	7.8, 7.8, 7.8
Increase.....	8.0, 7.8, 7.6 mean 7.8	2.6, 2.5, 2.5 mean 2.6
Pressure on (1) 6, on (2) 2 kgm./cm².		
Pressure increased by S_1.		
In dark.....	28.0, 31.6, 31.6	5.3, 5.3, 5.4
End (1) illuminated.	52.8, 52.6, 52.2	7.3, 7.5, 7.2
Increase.....	24.8, 21.0, 20.6 mean 22.1	2.0, 2.2, 1.8 mean 2.0
Pressure on (1) 18 kgm./cm²., on (2) kgm./cm².		
Pressure increased by S_2.		
In dark.....	20.0, 24.0, 26.0, 25.6	20.0, 20.0, 25.0, 25.0
End (1) illuminated.	40.0, 42.0, 48.0, 47.0	23.2, 30.3, 33.0, 34.5
Increase.....	20.0, 18.0, 22.0, 21.0 mean 20.2	3.2, 7.3, 8.0, 9.5 mean 7.0
Pressure on (1) 18 kgm./cm²., on (2) 6 kgm./cm².		
Pressure increased by S_2.		
In dark.....	25.4, 26.0, 26.4	68.9, 71.4, 74.0
End (1) illuminated.	48.8, 48.6, 47.0	81.3, 86.9, 88.5
Increase.....	23.4, 22.0, 20.6 mean 22.0	12.4, 15.5, 14.5 mean 14.5
Pressure on (1) 18 kgm./cm²., on (2) 13 kgm./cm².		

be a transmission of the pressure effect of secondary magnitude and importance which would not be detected except in more highly refined work. Then at least that part of the conduction that is brought about by increased pressures can not result from an increase in number of dynamically free electrons, and likewise that part of the increased conductivity that comes from a constant illumination as a result of increased pressure can not arise from free electrons at constant pressure everywhere within the crystal. Of course this argument requires that the increased pressure reacts against the fixed crystal structure and not against the free electrons. Now if the increased conductivity resulting from pressure on the crystal is not due to free electrons, it is difficult to justify conduc-

tion by free electrons at atmospheric pressure. The conclusion then seems unavoidable *that electrical conduction in crystals of metallic selenium can not be due to the traditional free electron.*

This conclusion need not be inconsistent with the result of Richardson and Brown[1] that the electrons inside a metal are free in the sense of the kinetic theory of gases, for our result was based upon work with highly conducting metals. Perhaps conduction in all non metals is like that in selenium crystals and dissimilar to that in the good conductors. It might be urged that the conductivity of selenium crystals is a function both of the number of free electrons and of a resisting medium through which they must pass. But this particular motion is inconsistent with the rapid transmission of the light-action along the crystal as was found.

The most satisfying unification of the experiments related that I have been able to conceive rests upon the hypothesis of conduction by electrons in semi-stable equilibrium. Scattered throughout the crystal structure are centers, perhaps atomic center, in which are associated charges of electricity in almost unstable equilibrium. Electrons free to move about in the structure as gas molecules move in enclosure do not exist. True these electrons are fixed in number and in position in the crystal structure, but the degree of their stability will vary with the agencies acting on the crystal. Electrical conduction consists essentially of a pulling out of these electrons from their moorings in the direction of the electrical stress. While out of position an electron might behave temporarily as a free electron in equilibrium with the heat and electrical forces about it. This process of conduction bears a little resemblance to the transfer of electricity in electrolytes.

The fact that Ohm's law does not hold for these crystals or metallic selenium generally is against the free electron hypothesis. The conductivity increases very greatly as the electrical forces in the line of conduction increase, until a saturation value of the conductivity is reached.

On this view increased pressure or tension on the selenium reduces the electrons to an average lower degree of stability. Thus a given fall of potential across the crystal will be able to dislocate a larger number of electrons from their fixed positions, or will be able to use them on an average a longer time before they recombine.

Similarly, light by some mechanism yet undiscovered lowers the degree of stability of the electrons throughout the crystal or further the mechanism controlled by light frees the most unstable electrons throughout the selenium. Thus as found if pressure is applied to any part of the crystal and any other part of the crystal is illuminated, that part of the

[1] Phil. Mag. (6), Vol. 16, p. 353, 1908, and Phil. Mag. (6), Vol. 18, p. 649, 1909.

crystal under pressure, and only that part, has its absolute light-sensitiveness increased. This merely means that at the place of great pressure the mechanism of light finds a greater number of electrons in such a low degree of stability that more of them can be kept in the free state.

It is still to be investigated how the light-action may be transmitted to a distance. It has occurred to the writer that it may be a change of crystalline structure, or an elastic vibration, or merely light diffusion.

DETERMINATION OF Ne FOR HYDROGEN FROM MEASUREMENTS OF BROWNIAN MOVEMENTS.

BY CARL F. EYRING.

INTRODUCTION.

VALUES of Ne for gaseous ionization have been determined by Townsend,[1] Franck and Westphal,[2] Fletcher, and others. By means of the measurement of the Brownian movements of a small oil drop, Fletcher[3] in 1911 made a direct determination of Ne for ionized air, and more recently[4] determined by the same method the value of the Avogadro constant N for air. Working with the same apparatus the writer attempted a determination of N for hydrogen, but obtained results which seem to indicate that the *ak* factor of the law of fall for hydrogen is different from that obtained by Millikan[5] for air. The determination of Ne was then undertaken since it does not involve the factor *ak*. The present article extends the Brownian movement method of Fletcher to the study of hydrogen with the view of testing the method in the case of gases other than air, and of determining directly the value of Ne for hydrogen.

§ I. EQUATIONS USED, APPARATUS, AND METHOD OF PROCEDURE.

The formula deduced by Fletcher[6] for the Avogadro constant N is

$$N = \frac{RTz^2}{6\pi\mu a k V_g^2 t_g}, \tag{1}$$

where R is the gas constant, T the absolute temperature, a the radius of the oil drop, μ the coefficient of viscosity of the gas through which it moves, t_g its time of fall under gravity, V_g its average velocity of fall, k a factor of the law of fall that depends on the radius of the drop and the mean free path of the gaseous molecules, and z a term, defined by equation (4) below, that comes from the solution of the integral that involves the Brownian movements of the oil drop.

[1] Proc. Roy. Soc., A, Vol. LXXX., p. 209, 1908.
[2] Verh. D. Phys. Ges., Juli 2, 1909.
[3] PHYS. REV., Vol. XXXIII., No. 2, Aug., 1911.
[4] PHYS. REV., Vol. IV., s. series, No. 5, Nov., 1914.
[5] PHYS. REV., Vol. I., s. series, p. 219, 1913.
[6] PHYS. REV., Vol. IV., s. series, No. 5, p. 442, Nov., 1914.

The motion of a sphere of charge e in an electrostatic field of intensity X is determined by

$$Xe = 6\pi\mu ak\frac{V_1 + V_2}{2}, \tag{2}$$

where V_1 is the velocity of fall and V_2 the velocity of rise against gravity.

Combining equations (1) and (2), the equation used for the determination of Ne is

$$Ne = \frac{RTz^2}{V_g^2 t_g X} \cdot \frac{V_1 + V_2}{2}. \tag{3}$$

All the quantities of the right hand member of this equation can be measured by experiment.

The apparatus, consisting of the lighting system, the observing system, the timing system, and the vessel containing hydrogen and suspended oil drops, is that described in detail by Fletcher,[1] with the addition of a hydrogen generating system and a slightly modified arrangement for blowing the oil drops. The hydrogen was generated from good chemicals, and was passed through potassium permanganate solution to remove impurities, and concentrated sulphuric acid and calcium chloride to remove moisture. The vessel was filled with hydrogen to the desired pressure, and the oil drops were blown by hydrogen from the atomizer into the vessel and between the condenser plates. Every precaution was taken to keep air from the chamber.

The method used to determine the quantities given in equation (3) by use of this apparatus has been described in detail by Fletcher,[2] and consists first of observing the Brownian movements of a very small oil drop (liquid vaseline) as it falls under the influence of gravity between two uncharged condenser plates, and then of observing its time of fall and rise under an electrostatic field of known intensity. The drop responds to the electric field when it contains one or more charges which it has caught from the ionized hydrogen. The ionization is produced by X-rays.

A scale of fifty divisions of known length is mounted in the eye piece of the observing telescope, and in observing the Brownian movements, the time is recorded as the drop crosses each division. When the full scale has been covered, the drop is raised by means of the electrostatic field, and observations are again taken. By a repetition of this process, as many as 1,666 observations were taken for a single drop (Table III., below). The average of all these times of fall is taken as t_g, and V_g is obtained from t_g and the length of the scale division b. The factor z of equation (3) is defined by the equation

[1] *L. c.*, p. 443.

[2] *L. c.*, p. 446.

$$z = \frac{2t_g}{\sqrt{\pi\tau}}\left(1 + \frac{1}{2z^2} + \frac{1}{4z^4} + \frac{3}{8z^6} + \cdots\right), \tag{4}$$

where

$$\tau = \frac{\overset{+}{t}_a - \overset{-}{t}_a}{2},$$

$\overset{+}{t}_a$ being the average of all times of fall greater than t_g, and $\overset{-}{t}_a$ being the average of all times of fall less than t_g.[1] The factor z which thus involves the Brownian movements of the oil drop, can be calculated to any desired degree of accuracy from equation (4).

The gas constant R is taken as 83.15×10^6. The electrostatic field X is determined by finding the difference of potential between the condenser plates by a Kelvin multicellular electrometer. The plate distance is 1.605 cm.

§ II. THE DATA.

The tables contain the average values which were computed from the observations on seven drops. Over 10,000 observations of the Brownian movements were made under good experimental conditions. Part I. of the tables contains the velocities of the drop in the electrostatic field. The quantities V_1', V_1'', V_1''', $\cdots$; V_2', V_2'', V_2''', $\cdots$ are the velocities of fall and rise respectively in the electrostatic field when the drop has 1, 2, 3, etc., charges. The values $V_1^{(n)} + V_2^{(n)}$, from which n is clearly determined, are divided by n to reduce to the condition of a single charge, and the average of all such values is used in equation (3). In Part II. of the tables, column 1 gives the constant distance over which time of fall under gravity was taken, column 8 gives the value of Ne calculated from equation 3, column 9 gives the number of observations, and the other columns give the average values computed from the Brownian movements of the drop.

TABLE I.

Drop 1.

Temperature 21.1° C. *Pressure* 30.12 *cm.*

Part I.

Volts = 993.1. $V_1' = .0378$. $V_1' + V_2' = .0678$ per charge.

$X = 2.062$. $V_2' = .0300$.

Part II.

b	t_g	V_g	t_a	$\overset{-}{t}_a$	τ	z	Ne	No. Obs.
.00922	2.079	.00444	2.552	1.693	.429	5.46	2.99×10^{14}	235
.01844	4.158	.00444	4.785	3.529	.628	7.46	2.79×10^{14}	167

[1] See Fletcher, *l. c.*, p. 441, for the values of $\overset{+}{t}_a$ and $\overset{-}{t}_a$ as deduced from the Brownian movement theory.

TABLE II.

Drop 2.

Temperature 20.8° *C.* *Pressure* 30.39 *cm.*

Part I.

Volts = 290.6. $V_1'' = .0232.$ $V_1'' + V_2'' = .0361.$

$X = .604.$ $V_2'' = .0129.$ $\therefore V_1' + V_2' = .0180$ per charge

Part II.

b	t_g	V_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	Ne	No. Obs.
.00922	1.863	.00495	2.220	1.531	.344	6.18	3.05×10^{14}	1019
.01844	3.724	.00495	4.240	3.284	.478	8.83	3.08×10^{14}	509
.02766	5.586	.00495	6.196	5.011	.592	10.70	3.05×10^{14}	337
.03688	7.448	.00495	8.191	6.790	.700	12.04	2.91×10^{14}	254

TABLE III.

Drop 3.

Temperature 20.5° *C.* *Pressure* 16.41 *cm.*

Part I.

Volts = 1,414.7. $V_1'' = .0832.$ $V_1' = .0449.$

$X = 2.938.$ $V_2'' = .0718.$ $V_2' = .0329.$

$V_1'' + V_2'' = .1551.$ $V_1' + V_2' = .0778.$

$\therefore V_1' + V_2' = .0777$ per charge.

Part II.

b	t_g	V_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	Ne	No. Obs.
.0118	1.963	.00601	2.254	1.672	.278	8.04	2.94×10^{14}	1666
.0236	3.926	.00601	4.370	3.542	.414	10.78	2.65×10^{14}	831
.0354	5.889	.00601	6.372	5.393	.489	13.66	2.84×10^{14}	550
.0472	7.852	.00601	8.389	7.277	.556	16.00	2.92×10^{14}	410
.0590	9.815	.00601	10.479	9.227	.626	17.85	2.91×10^{14}	315

TABLE IV.

Drop 4.

Temperature 21.0° *C.* *Pressure* 52.39 *cm.*

Part I.

Volts = 1,074.1. $V_1' = .0165.$ $V_1'' = .0308.$ $V_1''' = .0447.$

$X = 1.233.$ $V_2' = .0113.$ $V_2'' = .0251.$ $V_2''' = .0396.$

$V_1' + V_2' = .0278.$ $V_1'' + V_2'' = .0559.$ $V_1''' + V_2''' = .0843.$

$V_1^{IV} = .0575.$

$V_2^{IV} = .0527.$

$V_1^{IV} + V_2^{IV} = .1102.$

$V_1' + V_2' = .0278$ av. per charge.

Part II.

b	t_g	V_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	Ne	No. Obs.
.00937	3.640	.00254	4.320	3.069	.625	6.65	2.87×10^{14}	846
.01874	7.280	.00254	8.180	6.477	.851	9.85	3.15×10^{14}	421
.02811	10.920	.00254	12.024	9.913	1.055	11.75	2.99×10^{14}	278

TABLE V.

Drop 5.

Temperature 21.2° *C.* *Pressure* 52.78 *cm.*

Part I.

Volts = 1,044.8. $V_1' = .0138.$ $V_1''' = .0337.$ $V_1^{IV} = .0422.$

$X = 2.170.$ $V_2' = .0060.$ $V_2''' = .0257.$ $V_2^{IV} = .0346.$

$V_1' + V_2' = .0198.$ $V_1''' + V_2''' = .0594.$ $V_1^{IV} + V_2^{IV} = .0768.$

$V_1^{V} = .0537.$ $V_1^{VII} = .0734.$

$V_2^{V} = .0462.$ $V_2^{VII} = .0651.$

$V_1^{V} + V_2^{V} = .0999.$ $V_1^{VII} + V_2^{VII} = .1385.$

$V_1' + V_2' = .0198$ av. per charge.

Part II.

b	t_g	V_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	Ne	No. Obs.
.01874	4.770	.00393	5.198	4.335	.431	12.54	2.39×10^{14}	551
.03748	9.540	.00393	10.068	8.993	.537	19.90	3.01×10^{14}	276
.05622	14.310	.00393	15.076	13.631	.722	22.40	2.54×10^{14}	178

TABLE VI.

Drop 6.

Temperature 20.8° *C.* *Pressure* 55.30 *cm.*

Part I.

Volts = 1,118.1. $V_1' = .0243.$ $V_1'' = .0440.$ $V_1''' = .0625.$

$X = 2.320.$ $V_2' = .0140.$ $V_2'' = .0337.$ $V_2''' = .0526.$

$V_1' + V_2' = .0383.$ $V_1'' + V_2'' = .0777.$ $V_1''' + V_2''' = .1153.$

$\therefore V_1' + V_2' = .0385$ av. per charge, and $\dfrac{V_1' + V_2'}{X} = .0166.$

Volts = 1,123.8. $V_1' = .0233.$ $V_1'' = .0426.$ $V_1''' = .0611.$

$X = 2.338.$ $V_2' = .0154.$ $V_2'' = .0345.$ $V_2''' = .0543.$

$V_1' + V_2' = .0387.$ $V_1'' + V_2'' = .0781.$ $V_1''' + V_2''' = .1154.$

$\therefore V_1' + V_2' = .0388$ av. per charge and $\dfrac{V_1 + V_2}{X} = .0166.$

$$\therefore \frac{V_1 + V_2}{X} = .0166 \text{ av.}$$

Part II.

b	t_g	V_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	Ne	No. Obs.
.01674	4.679	.0040	5.191	4.155	.518	10.27	2.83×10^{14}	446
.03748	9.358	.0040	10.145	8.667	.739	14.33	2.75×10^{14}	221

TABLE VII.

Drop 7.

Temperature 20.8° *C.* *Pressure* 55.30 *cm.*

Part I.

Volts = 1,123.8. $V_1' = .0233.$ $V_1'' = .0426.$ $V_1''' = .0611.$

$X = 2.338.$ $V_2' = .0154.$ $V_2'' = .0345.$ $V_2''' = .0543.$

$V_1' + V_2' = .0387.$ $V_1'' + V_2'' = .0781.$ $V_1''' + V_2''' = .1154.$

$V_1' + V_2' = .0388$ av. per charge. $\dfrac{V_1' + V_2'}{X} = .0166.$

Volts = 1,121.4. $V_1'' = .0421.$ $V_1'' + V_2'' = .0773.$

$X = 2.330.$ $V_2'' = .0352.$ $V_1' + V_2' = .0386$ per charge.

$$\frac{V_1 + V_2}{X} = .01658. \quad \therefore \quad \frac{V_1 + V_2}{X} = .01659 \text{ av.}$$

Part II.

b	t_g	V_g	$\dot{t}_a$	$\bar{t}_a$	τ	s	Ne	No. Obs.
.01874	5.143	.00365	5.762	4.570	.596	9.78	2.83×10^{14}	379
.03748	10.286	.00365	11.156	9.475	.840	13.88	2.85×10^{14}	188

TABLE VIII.

A Summary of the Values of Ne and the Corresponding Number of Observations.

Drop.	Ne ÷ 10^{14}	No. of Obs.	Drop.	Ne ÷ 10^{14}	No. of Obs.
1	2.99	235		2.87	846
	2.77	167	4	3.15	421
				2.99	278
	3.05	1019			
2	3.08	509		2.39	551
	3.05	337	5	3.01	276
	2.91	254		2.54	178
	2.94	1666	6	2.83	446
	2.65	831		2.75	221
3	2.84	550			
	2.92	410	7	2.83	379
	2.91	315		2.85	188

Assigning weights to the values of Ne according to the number of observations, the average value

$$\text{Ne} = 2.880 \times 10^{14}$$

is obtained. The value of Ne obtained from electrolysis is 2.896×10^{14}. The average value differs from this by .5 per cent.

The results of this investigation lead, therefore, to the conclusion that the Brownian movement method holds for gases other than air, and that the molecules of ionized hydrogen carry the same charge as the hydrogen ions of electrolysis.

This investigation was made in the Physical Laboratory of the Brigham Young University on the suggestion and with the generous assistance of Professor H. Fletcher.

FLUORESCENCE OF THE URANYL SALTS UNDER X-RAY EXCITATION.

BY FRANCES G. WICK.

THE fluorescence spectrum characteristic of the uranyl salts is known to consist of several narrow bands, sometimes as many as seven, regularly arranged and sharply defined. An extended study of these salts has recently been made by Nichols and Merritt[1] with a view to discovering whether the fluorescence bands in a given salt are independent of each other, or whether they form a series so connected that any agency which excites one of the bands excites the others also. In this investigation, light of different wave-lengths was used for excitation and the fluorescence, in each case, was carefully observed to determine whether or not certain regions of the spectrum might excite the bands independently of each other.

A variation of the form of the fluorescence curve was found with different exciting lights. This, however, was explained by the fact that the absorption of both the exciting light and the fluorescent light varies with wave-length. The fluorescence bands for which the absorption is greatest appear weaker when the exciting light penetrates to a great distance in the salt than when it is absorbed by a comparatively thin surface layer. The conclusion reached by Nichols and Merritt is that for a layer of the salt so thin that absorption would be negligible, the form of the fluorescence spectrum would be the same for all excitations and the observed distribution of energy would correspond to the actual distribution. The fluorescence of these salts appears to be due to vibrations set up in a single connected mechanism and any agency which excites one of the bands in a given salt excites the others also.

It seemed of interest, in this connection, to determine whether or not the spectra of the fluorescence excited by X-rays differed in any way from that excited by other sources. With this end in view, a series of experiments was undertaken, at the suggestion of Professors Nichols and Merritt, upon some uranyl salts freshly prepared for them. Most of these salts could be excited to fluorescence in varying degrees of intensity by the violet light of the carbon arc.

[1] Nichols and Merritt, PHYS. REV., Vol. 33, p. 354, 1911.

In order to determine which of the specimens were excited to fluorescence by X-rays, a preliminary test was made, the source of excitation being X-rays from a water-cooled tube with a parallel spark gap of from five to eight inches. The tube was run by current from an induction coil, to the primary of which was connected a mercury interrupter, no attempt being made to keep the current and voltage constant.

The intensity of the fluorescence excited in the different salts varied greatly, being, in every case, much less than that excited by the violet light of the arc. The salts under observation were roughly divided into three groups with respect to the brightness of the fluorescence excited. These groups are as follows:

GROUP 1.

Salts in which the Fluorescence is Relatively Bright.

Uranyl cæsium sulphate.
Uranyl potassium sulphate.
Uranyl rubidium sulphate.
Uranyl sodium sulphate.
Uranyl potassium nitrate.

GROUP 2.

Salts in which the Fluorescence is Faint.

Uranyl acetate.
Uranyl ammonium acetate.
Uranyl ammonium chloride.
Uranyl nitrate.
Uranyl nitrate tri-hydrate.

GROUP 3.

Salts which were not Excited to Fluorescence.

Uranyl acetate.
Uranyl ammonium fluoride.
Uranyl antimony tartarate.
Uranium fluoride.
Uranyl iodate.
Uranyl oxalate.
Uranyl potassium fluoride.
Uranyl tartarate.
Uranyl potassium tartarate.
Uranyl thallous sulphate.

The same salts were later exposed to X-rays from a Coolidge tube running at high voltage and current. The fluorescence of the first two

groups was greatly increased and the third group all showed some fluorescence except the following:

Uranyl antimony tartarate.
Uranium fluoride.
Uranyl potassium tartarate.
Uranyl thallous sulphate.

These salts showed no fluorescence under excitation by light. The variation in the intensity of the other salts under light and X-ray excitation seemed to follow approximately the same order.

In order to determine whether the fluorescence excited by X-rays differed, in any way, from that excited by the violet light of the arc, a comparison of the spectra of the fluorescence excited by the two sources was made. The apparatus was arranged as shown in Fig. 1. A thin

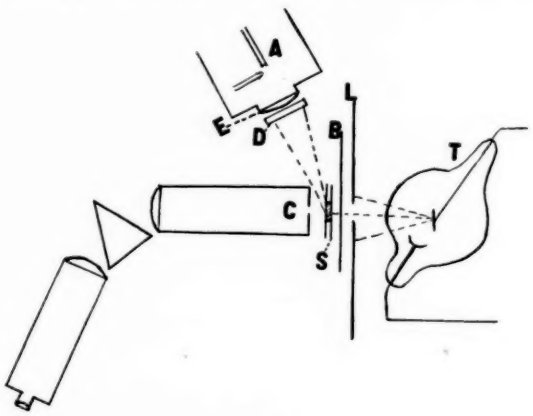

Fig. 1.

layer of the salt to be observed was mounted between two glass plates and placed at *S*, a short distance in front of the collimator slit *C*, of a spectrometer. X-rays from a water-cooled tube, *T*, were allowed to pass through the specimen, the fluorescence being observed from the side of emergence of the X-rays. The rays were so penetrating that the fluorescence of the incident and emergent sides of the specimen did not differ perceptibly. A heavy lead screen, *L*, was used for protection. A right-angled arc, *A*, was set up in such a way that the light from the arc, after passing through a converging lens, *E*, and a heavy blue glass, *D*, could be thrown obliquely on the specimen, *S*, without changing any of the adjustments.

The first salt to be examined in this way was uranyl cæsium sulphate. The spectrum of the fluorescence excited by the arc consisted of six bands which could be easily observed. The bands toward the violet end

of the spectrum, *a*, *b*, *c*, and *d* were bright, each having a sharply defined crest, the intensity fading off gradually toward the longer wave-lengths, and more abruptly toward the shorter wave-lengths—the usual form of the fluorescence bands. The red bands, *e* and *f*, were broad and dim without any well-defined crest.

Excitation of this salt by X-rays produced fluorescence of such low intensity that it was necessary for the observer to be in absolute darkness for some time before attempting to make any settings. The difficulty of making observations was increased by the fact that it was possible to run the X-ray tube with safety for only short intervals of time. Bands *a*, *b*, *c*, and *d*, were similar to the corresponding bands excited by light,

Fluorescence Bands of Uranyl Salts.

	Wave-length of Bands.					
	a	*b*	*c*	*d*	*e*	*f*
Uranyl cæsium sulphate.						
Light excitation.....	4866	5080	5320	5560	5860	6190
X-ray excitation.....	4863	5073	5325	5565	....	....
Uranyl potassium sulphate.						
Light excitation.....	4918	5137	5385	5610	5900	6228
X-ray excitation.....	4908	5132	5388	5615	....	....
Uranyl rubidium sulphate.						
Light excitation.....	4915	5140	5380	5613	5910	
X-ray excitation.....	4920	5135	5378	....	....	
Uranyl sodium sulphate.						
Light excitation.....	4910	5114	5375	5605	5903	
X-ray excitation.....	4915	5118	5378	....	....	
Uranyl potassium nitrate.						
Light excitation.....	4870	5096	5332	5595	5890	6197
X-ray excitation.....	4865	5110	5337	5590	....	....
Uranyl nitrate trihydrate.						
Light excitation	4880	5098	5350	5610	5905	6275
X-ray excitation.....	4861	5100	5370	....	....	....

the only difference observable being one of brightness. Bands *e* and *f* which were broad and dim under light excitation, did not appear under excitation by X-rays.

The results of measurements of the wave-lengths of the crests of these

bands under the two sources of excitation are shown in the accompanying table. The wave-lengths of the crests of the corresponding bands are found to be the same within the limits of observational errors. The difference is not so great as that between the individual settings upon the same crest. Because of the low intensity of the fluorescence under X-rays, it was necessary to have the collimator slit wider open than is desirable for accurate determination of wave-length. In each case, several settings were made and the wave-length corresponding to the average determined from a calibration curve.

As a check upon these results, the indicator in the eyepiece of the spectrometer was repeatedly set upon the crest of one of the bands excited by one source, then the excitation was changed, without changing any of the adjustments, and the indicator was found to have exactly the same position with reference to the band.

Measurements of this kind were made upon all the salts given in the table. The only difference which could be detected in the position and character of the bands when the source of excitation was changed, was such as might have been due to a change in intensity of fluorescence. In every case, the intensity of the bands was less and the number of bands observed fewer under X-ray excitation. The bands which were missing were those in the red end of the spectrum which were comparatively broad and dim under excitation by light.

These results are in agreement with the conclusions reached by Nichols and Merritt that the fluorescence of the salts is due to a mechanism the parts of which are so related that any source which excites one of the bands excites the others, also.

An attempt was made to photograph the fluorescence spectra excited by more powerful X-rays from a Coolidge tube running at a voltage of 45 kilovolts and a current of 30 milli-amperes. An exposure amounting to 30 minutes made by a series of excitations of from 30 to 45 seconds duration with sufficient time between to allow the target to cool, produced no satisfactory results.

Later experiments showed that the intensity of fluorescence was greatly increased by raising the voltage of the tube but the safe time of running the tube was shorter. Further attempts at photographing the spectrum did not seem feasible.

PHOSPHORESCENCE OF THE URANYL SALTS AT LOW TEMPERATURES.

In order to make some observations upon the fluorescence of uranyl potassium sulphate at low temperatures, the specimen was placed in a glass tube and lowered into an unsilvered Dewar bulb containing liquid

air. At this temperature, under the excitation of the violet light of the arc, the bands of the fluorescence spectrum showed the characteristic resolution into narrower bands.[1] This change could not be observed under X-ray excitation, probably because of the low intensity of the fluorescence.

At the low temperature acquired, the salt became phosphorescent, the effect being much brighter and of longer duration when X-rays were used for excitation than when the violet light of the arc was used at the same temperature. The salt is not perceptibly phosphorescent at room temperature.

The decay of the phosphorescence was at first very rapid, then much slower. Some observations were made to determine the general shape of the decay curve.

The apparatus was set up as shown in Fig. 2.

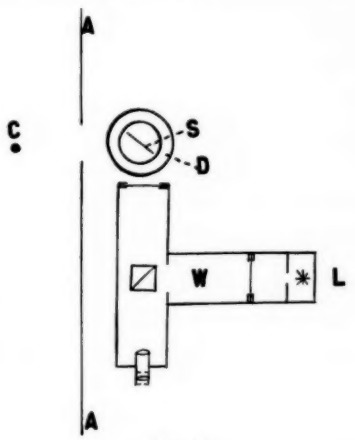

Fig. 2.

A specimen of uranyl potassium sulphate, *S*, was placed in a test-tube surrounded by liquid air in an unsilvered Dewar bulb, *D*, and the X-rays from a Coolidge tube, *C*, were allowed to strike it. For measurement of the intensity of the phosphorescence, a Weber photometer, *W*, was used, the comparison source being a low candle-power tungsten lamp, *L*. A thick lead screen, *A*, was used for protection.

To produce phosphorescence, the specimen was exposed to the X-rays for two seconds, the time being accurately measured by a device attached to the apparatus for use in X-ray photography. The tube was running at 60 kilo-volts and 11.8 milli-amperes. A setting of the photometer was made when the specimen was under excitation, then the comparison field was cut down to a definite intensity and the time necessary for the phosphorescence to be reduced to this value was measured by means of a stop watch. The time was taken, in this way, for reduction to a number of different intensities. The decay curve obtained is shown in Fig. 3.

The decay was, at first, very rapid, then very slow, as is indicated by the shape of the curve. The faintness of the phosphorescence after the first very rapid decay, made it seem unwise to attempt to pursue this study with more refined apparatus for the measurement of time.

A number of the other uranyl salts were found to show this same

[1] Nichols and Merritt, PHYS. REV., Vol. 33, p. 372, 1911.

peculiarity at the temperature of liquid air: under excitation of violet light, they were brilliantly fluorescent but showed little phosphorescence; under excitation by X-rays, the fluorescence was comparatively faint but the phosphorescence was much more pronounced.

The fact that the salts are so much more phosphorescent under excitation by X-rays than by light may be explained by a difference in

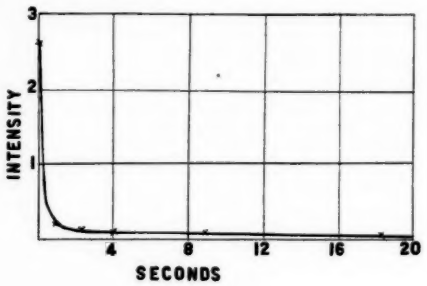

Fig. 3.

Decay of phosphorescence of uranyl-potassium sulphate after a two-second exposure to X-rays from a Coolidge tube.

absorption. When radiations from the exciting source were thrown normally upon a thin specimen of one of the salts, the fluorescence on the side of incidence was much more intense than on the side of emergence for excitation by light, but there was no perceptible difference in the intensity of the two sides with X-rays as the source of excitation.

Nichols and Merritt[1] found that the phosphorescence excited in Sidot Blende by cathode rays is less intense and more fleeting than that excited in the same substance under light excitation. This was accounted for by a difference in the penetration of the rays, light rays being more penetrating than cathode rays. The excitation by light is confined to a thin surface layer; under the more penetrating light rays the effect extends to a greater depth, resulting in a more gradual decay.

This explanation suggested the idea that the X-rays being more penetrating to the uranyl salts than light, the effect produced by them is deeper and lasts longer.

CONCLUSIONS.

The conclusions which may be drawn from the experiments described in this paper are as follows:

1. The fluorescence excited in the uranyl salts by X-rays differs from that excited by light in intensity only. The greater absorption of these salts for light than for X-rays accounts for the difference in intensity of fluorescence under the two sources.

[1] Nichols and Merritt, PHYS. REV., Vol. 27, p. 349, 1908.

2. The phosphorescence following excitation by light is less intense and of shorter duration than that excited by X-rays. The difference in penetration of the two kinds of radiation seems to explain this, the more penetrating X-rays producing a phosphorescence which is more intense and of longer duration than that following the less penetrating light rays.

These experiments were carried on at Cornell University and I wish to express my sincere thanks to Professors Nichols, Merritt and Shearer for their interest and help and for their kindness in putting at my disposal the facilities of the laboratory.

VASSAR COLLEGE,
POUGHKEEPSIE, N. Y.

INTEGRATION OF THERMODYNAMIC EQUATIONS FOR AN IMPERFECT GAS.

BY SANFORD A. MOSS.

THE two laws of thermodynamics give certain differential equations connecting the heat-capacities of a substance with its pressure-volume relations, which have been integrated in special cases. A general integration is here made.

Total Heat.—The mathematical work is most readily accomplished by the use of " total heat," H, as the principal dependent variable. This is defined as the number of heat units added per unit of flow when a stream of fluid passes from a standard region to a region at a given pressure and temperature. It includes intrinsic or internal energy change due to molecular heat storage, dU, plus energy which has been supplied but which has not been added to the fluid in question. This latter represents work necessarily performed on the external universe, first, due to direct expansion $Apdv$, and second, required to force the fluid into the given region and out of the standard region, $Avdp$. (The sum of the first two terms is heat added to fluid in a closed envelope without flow, dQ, and we have $dH = dQ + Avdp$.) Now

$$vdp + pdv = d(pv)$$

so that

$$dH = dU + Ad(pv).$$

Since both terms on the right are exact functions, it follows that total heat is an exact function which has a fixed value for each condition, defined for instance by values of p and T, regardless of the manner in which the condition was reached. (This is really a form of statement of the First Law of Thermodynamics.) Total heat leads to simpler mathematical work than Q, which is not an exact function. It is in very general use by engineers. We will obtain general expressions for total heat for the gaseous state and for the liquid state, in terms of pressure and temperature. Then substitution of saturation pressure and temperature gives total heat for saturated vapor and saturated liquid. The difference between these two is latent heat of vaporization.

Notation and Definitions.—Quantities of heat, energy, total heat, etc., in heat units such as B.T.U. (pound-degree Fahrenheit) or calories

(kilogram-degree Centigrade). Pressures in pounds per square foot or kilograms per square centimeter. Volumes in cubic feet or cubic centimeters.

A = reciprocal of mechanical equivalent of heat.

T = absolute temperature.

p = absolute pressure.

H = total heat as already explained. The change in H is heat added per unit weight when a substance flows from a point at one pressure and temperature to a point at another pressure and temperature. We arbitrarily take H as measured above liquid at p_0 and T_0, where T_0 is the triple point of water (freezing point at saturation pressure) which is practically 273.1° C. or 459.6° F., and p_0 is the saturation pressure of the substance being considered, at this arbitrary temperature.

U = internal or intrinsic energy measured above same point as H. Having defined H as an observed quantity as above we may define U by the relation $dH = dU + Ad(pv)$. We may take the first law of thermodynamics as being "U is an exact function," whence H is exact also, so that we can integrate directly, giving $H = U + Apv - Ap_0v_0$. Beyond we deduce various values of H, and values of U may be obtained from them by deducting $Apv - Ap_0v_0$. U is therefore given no further attention.

Q = heat added to unit weight when at rest in a closed envelope. From the above aspect of the first law of thermodynamics as well as the laws of hydrodynamics, it follows that $dH = dQ + Avdp$ and $dQ = dU + Apdv$.

ϕ = entropy, measured above same point as H. It is defined by the relation $d\phi = dQ/T$. The second law of thermodynamics may be taken as being "ϕ is an exact function." We have $dH = Td\phi + Avdp$ and $Td\phi = dU + Apdv$.

c_p = specific heat at constant pressure, defined as being $(dQ/dT)_p$ as well as $(dH/dT)_p$.

c_{p0} = value of c_p approached as pressure approaches 0. In general c_{p0} is a function of T.

c_v = specific heat at constant volume, defined as being $(dQ/dT)_v$. It follows

$$\left(\frac{dH}{dT}\right)_v = c_v + Av\left(\frac{dp}{dT}\right)_v.$$

The relations deduced throughout, unless specifically excepted, apply to either gaseous or liquid state. Where

distinction between the two states is necessary, $vHU\phi c_p c_{p0} c_v$ will refer to gaseous state and $v'H'U'\phi' c_p' c_v'$ will refer to the liquid state. c_p' will be specific heat of liquid at the reference pressure p_0. In general c_p' is a function of T. Many of the relations also apply to the solid state, and when vH, etc., and $v'H'$, etc., appear, the relations may apply to gaseous and solid states. However this extension to solid state will not be definitely worked out.

μ = Joule-Thomson coefficient, defined as being $(dT/dp)_H$. From the general relation

$$\left(\frac{dH}{dp}\right)_T \left(\frac{dp}{dT}\right)_H \left(\frac{dT}{dH}\right)_p = -1$$

it follows that

$$\left(\frac{dH}{dp}\right)_T = -\mu c_p.$$

q = total heat of saturated liquid, that is, value of H' for saturation values of p and T. We will consider this as true total heat, and for exactness will include a small volume term, usually ignored. True total heat of liquid for any values of p and T, not necessarily saturation, can be expressed just as is total heat of gas beyond, giving

$$H' = \int_{T_0}^{T} c_p' dT - AT^2 \int_{p_0}^{p} \left(\frac{d\{v'/T\}}{dT}\right)_p dp_T.$$

The last term can be written

$$-AT \int_{p_0}^{p} \left(\frac{dv'}{dT}\right)_p dp_T + A \int_{p_0}^{p} v' dp_T.$$

Here c_p' is the specific heat of liquid as a function of T for $p = p_0$. If p and T have saturation values the above expression becomes the general value for q. Or if c_p' and v' and the variation are along the saturation curve we have a similar expression. With no error (except near the critical point) the liquid volume v' may be taken constant so that we have as an approximate general expression for total heat of liquid in general,

$$H' = \int_{T_0}^{T} c_p' dT + Av'(p - p_0).$$

Here c_p' is the specific heat of liquid as a function of T, which must be independent of pressure when v' is constant (according

to (7) beyond). If p and T have saturation values the last expression becomes a closely approximate value of q. That is

$$q = \int_{T_0}^{T} c_p' dT + Av'(p - p_0)$$

where p and T are saturation values.

We will not make the further common approximation of omitting the small term $Av'(p - p_0)$. This is usually done in steam tables without good reason. Omission of the term in steam turbine and engine computation gives energy of turbine minus energy of boiler feed pump. The complete expression for q gives energy of the turbine without this deduction. Total heat of saturated steam is often loosely defined as $r + \int_{T_0}^{T} c_p' dT$, which gives a value slightly different from total heat of superheated steam on the saturation line. This is avoided by the above definition of q.

n = entropy of saturated liquid, that is, value of ϕ' for saturation values of p and T. Entropy of liquid for any values, not necessarily saturation, as shown beyond for gases, is

$$\phi' = -A \int_{p_0}^{p} \left(\frac{dv'}{dT}\right)_p dp_T + \int_{T_0}^{T} \frac{c_p'}{T} dT,$$

where c_p' is specific heat of liquid as a function of T for $p = p_0$. If, however, p and T have saturation values, this becomes the the general expression for n. Or if c_p' and v' and the variation are along the saturation curve we have a similar expression. As in the case of q, we can take v' as constant (except near the critical point). Then entropy of the liquid is independent of pressure, and for any temperature entropy of saturated liquid is the same as entropy of liquid for all pressures. We have therefore as a closely approximate expression

$$n = \phi' = \int_{T_0}^{T} \frac{c_p'}{T} dT.$$

This is the expression usual in steam tables.

r = latent heat of evaporation. Value of $H - H'$ or $H - q$ for saturation values of p and T.

r_0 = value of r at p_0 and T_0.

λ = total heat of saturated steam or value of H for saturation conditions. $\lambda = q + r$.

u = volume increase at evaporation. Value of $v - v'$ for saturation values of p and T.

$f(T)$ = expression giving pressure of saturated vapor at temperature T. That is, the vapor pressure equation is $p = f(T)$.

$f'(T)$ = derivative of $f(T)$ with respect to T or value of dp/dT where p is saturation pressure.

Fundamental Differential Equations.—We will list some well-known relations which are the basis of our discussion. From the definition of ϕ and H

$$d\phi = \frac{1}{T} dH - A \frac{v}{T} dp.$$

By dividing by dT and putting p constant

$$\left(\frac{d\phi}{dT}\right)_p = \frac{c_p}{T}. \tag{1}$$

By dividing by dp and putting T constant

$$\left(\frac{d\phi}{dp}\right)_T = \frac{1}{T}\left(\frac{dH}{dp}\right)_T - A \frac{v}{T}. \tag{2}$$

By differentiating (1) and (2) we obtain values for $d^2\phi/dpdT$ which we can equate since ϕ is exact, yielding (after cancelling values of $d^2H/dpdT$ since H is exact)

$$\left(\frac{dH}{dp}\right)_T = Av - AT\left(\frac{dv}{dT}\right)_p. \tag{3}$$

An equivalent expression is

$$\left(\frac{dH}{dp}\right)_T = -AT^2\left(\frac{d\{v/T\}}{dT}\right)_p. \tag{4}$$

This is our fundamental relation between heat contents and volume. We later integrate it so as to obtain both v in terms of H and H in terms of v.

An auxiliary relation is found by multiplying each side of (3) by $(dp/dv)_T$,

$$\left(\frac{dH}{dv}\right)_T = Av\left(\frac{dp}{dv}\right)_T + AT\left(\frac{dp}{dT}\right)_v. \tag{5}$$

A special case of this equation is the well-known Clapeyron equation for a body of wet vapor,

$$\frac{r}{u} = ATf'(T). \tag{6}$$

By differentiation of (3) with respect to T, with p constant

$$\left(\frac{dc_p}{dp}\right)_T = -AT\left(\frac{d^2v}{dT^2}\right)_p. \tag{7}$$

This has been called the " Clausius relation." From (2) and (3) we have

a general relation giving entropy in terms of volume

$$\left(\frac{d\phi}{dp}\right)_T = -A\left(\frac{dv}{dT}\right)_p. \tag{8}$$

By differentiation of (5) with respect to T with v constant

$$\left(\frac{dc_v}{dv}\right)_T = AT\left(\frac{d^2p}{dT^2}\right)_v.$$

c_v might be obtained by integration of this equation in the same way as we later obtain c_p from (7). However it will usually be more convenient to first obtain c_p and then obtain c_v from a relation which we deduce by combining

$$\left(\frac{dH}{dT}\right)_v = c_v + Av\left(\frac{dp}{dT}\right)_v$$

and

$$\left(\frac{dH}{dT}\right)_p = \left(\frac{dH}{dT}\right)_v + \left(\frac{dH}{dv}\right)_T\left(\frac{dv}{dT}\right)_p$$

with (5), which gives

$$c_v = c_p - AT\left(\frac{dp}{dT}\right)_v\left(\frac{dv}{dT}\right)_p$$

$$= c_p + AT\left(\frac{dv}{dT}\right)_p^2 \Big/ \left(\frac{dv}{dp}\right)_T.$$

Beyond we deduce various values of c_p and values of c_v may be obtained from them by use of this expression. c_v is therefore given no further consideration.

The Joule-Thomson coefficient μ may also be obtained from the value of c_p by use of the relation

$$(dH/dp)_T = -\mu c_p$$

and (3) which gives

$$\mu = -\frac{Av - AT\left(\frac{dv}{dT}\right)_p}{c_p} = \frac{AT^2\left(\frac{d\{v/T\}}{dT}\right)_p}{c_p}.$$

μ is therefore given no further consideration.

We have as a general relation

$$dH = c_p dT + \left(\frac{dH}{dp}\right)_T dp.$$

If we substitute for $(dH/dp)_T$ from (3) and also stipulate that the variation of H and p shall be along the saturation curve, we have

$$\frac{d\lambda}{dT} = c_p - Af'(T)\left\{T\left(\frac{dv}{dT}\right)_p - v\right\}. \tag{9}$$

We may also substitute for $f'(T)$ from (6)

$$\frac{d\lambda}{dT} = c_p + \frac{r}{T} - \frac{r}{u}\left(\frac{dv}{dT}\right)_p + \frac{r}{T}\frac{v'}{u}. \tag{10}$$

This has been called " Planck's equation." The last term is very small and may be neglected. The above form is exact on the basis of our use of heat of liquid and gas at saturation as true " total heat." Other small terms occur when this is not done.

Relation Between Total Heat and Volume.—As remarked, (4) gives a fundamental relation between total heat and volume, and tables or curves from computation or experiment giving these quantities must have the mutual relation shown by (3) or (4). Some well-known steam tables give properties of superheated steam on basis of formulas which confessedly do not satisfy the desired relation. Hence comparison of values of the two sides of (3) computed by interpolation and differences shows some disagreement.

Total Heat and Entropy of an Imperfect Gas from Volume.—By integration of (4) with respect to p, maintaining T constant, we obtain a value for H if we can express the integral of the right hand member. There are two ways in which this might be done.

If there existed a good set of experimental values of volume for a wide range of pressures and temperatures they would give the desired values of H. However such values of volume do not now exist.

The other way is by use of values of volume given by a characteristic equation or equation of state. Many such equations have been proposed for steam and other gases on empirical or semi-rational grounds. We will obtain expressions for total heat and specific heat implied by any such equation.

The general expression for H from integration of (4) is

$$H = -AT^2 \int \left(\frac{d\{v/T\}}{dT}\right)_p dp + F(T). \tag{11}$$

This does not completely determine H since it involves $F(T)$ an arbitrary function of T not determined by considerations of volume and which must be evaluated by other means. The integral in (11) is obtained by differentiating v/T with respect to T, considering p a constant and then integrating with respect to p considering T a constant. The order of these operations is immaterial. The evaluation of the integral in this way satisfies every requirement so far as volume relations or characteristic equations are concerned, and the function $F(T)$ must be determined by wholly different considerations. For instance, $F(T)$ could be established by knowledge of values of H for various values of T at a particular value of p.

The fundamental differential equation (3) or (4) uses values of volume v to give variation of total heat H with pressure, from point to point along each isotherm. Hence if we have values of v in general, and an initial value of H at any one point on an isotherm, we can determine all other values of H along that isotherm. We cannot, however, from knowledge of v alone pass from one isotherm to the next, but must have as additional information one initial value of H on each isotherm, corresponding to some pressure or curve of pressures.

The general expression for c_p corresponding to the above value for H is

$$c_p = -AT\int\left(\frac{d^2v}{dT^2}\right)_p dp_T + F'(T). \qquad (11A)$$

We will use the notation $\int f(p, T)dp_T$ to denote partial integration, that is, integration with respect to p on the assumption that T is a constant. This operation performed on $(df_1/dp)_T$ yields f_1, except for a function of T. That is to say, the partial integral must be completed by addition of a function of T, arbitrary so far as it is concerned.

It is to be noted that this operation $\int \cdots dp_T$ is commutative with any other operations (such as differentiations or integrations) in which p is constant. That is

$$(d\{\int f dp_T\}/dT)_p = \int (df/dT)_p dp_T.$$

We may write such an expression as (11) in the form of a definite integral, that is, one with limits. In such a definite integral the variable which is kept constant must be left with its general value in both upper and lower limits. This is T in the case of (11). The variable with respect to which the integration is performed is replaced respectively by the values given by the upper and lower limits. Usually it will be left with the general value in the upper limit of the integral, and will have some particular value in the lower limit. In the case of (11) the upper limit is obtained later by putting p as p and the lower limit by putting p as 0, in both cases leaving T as T. The term from the lower limit therefore gives the requisite function of T only which must be added after the partial integration with respect to p.

We next determine entropy just as we did total heat. We integrate (8) giving in general

$$\phi = -A\int\left(\frac{dv}{dT}\right)_p dp_T + G(T). \qquad (12)$$

Just as in the case of total heat, knowledge of v only gives variation along each isotherm, and in order to pass from one isotherm to another we

must have additional information. This is given by similar information for total heat, the relation being given by (1), so that assumption of the value of $F(T)$ fixes $G(T)$. From (11A) and (1)

$$\left(\frac{d\phi}{dT}\right)_p = -A\int\left(\frac{d^2v}{dT^2}\right)_p dp_T + \frac{F'(T)}{T}.$$

Comparison of this with result of differentiation of above value of ϕ shows that

$$G'(T) = \frac{F'(T)}{T},$$

so that

$$\phi = -A\int\left(\frac{dv}{dT}\right)_p dp_T + \int\frac{F'(T)}{T}dT. \qquad (13)$$

Total Heat and Entropy from Volume and Specific Heat at Zero Pressure. —Callender has proposed to obtain the additional knowledge above referred to by the assumption that the specific heat at pressure " zero " is constant, and Goodenough has empirically adopted a certain variable value instead. We will therefore express total heat as given by (11) in terms of c_{p0} the value of c_p for $p = 0$. In general we suppose c_{p0} a function of T.

We do this by writing (11) as a definite integral, as already mentioned. We may make the lower limit $p = 0$ and this has the effect of adding a function of T only which is permissible. The definite integral now vanishes for $p = 0$ for all values of T. If we further add a function of T whose derivative is the desired value of c_{p0} we satisfy the condition that c_p shall have this value for $p = 0$. The expression thus obtained is a function of p and T. We may add as a constant of integration the result of substitution of p_0 and T_0 for p and T in this function so that it will vanish for p_0 and T_0. We also add the arbitrarily selected initial value of H at p_0 and T_0, which is r_0. This value is then assumed at p_0 and T_0. As a result of thus selecting functions of T only and constants of integration, the general integral (11) of equation (4) gives as the general value of total heat, in terms of specific heat of gas at zero pressure,

$$H = r_0 - A\left[T^2\int_0^p\left(\frac{d\{v/T\}}{dT}\right)_p dp_T\right]_{p_0T_0}^{pT} + \int_{T_0}^{T} c_{p_0}dT. \qquad (14)$$

The integral within the brackets is the result of partially integrating $(d\{v/T\}/dT)_p$ with respect to p, counting T as a constant, and then substituting the limits p and 0 for the variable of integration p. T is to be maintained as the general value T. The resulting expression within the brackets is then to have first p and T and then p_0 and T_0 substituted as limits, for p and T.

It may be remarked that the above expression selects as the arbitrary function of (11),

$$F(T) = AT^2 \int^0 \left(\frac{d\{v/T\}}{dT}\right)_p dp_T + \int_{T_0}^{T} c_{p_0} dT. \tag{15}$$

In addition there are constants of integration involving p_0, T_0, etc.

The bracket in (14) involves four terms, with p and T, 0 and T, p_0 and T_0, 0 and T_0 successively substituted for p and T; in the partial integral of $(d\{v/T\}/dT)_p$ with respect to p with T constant. The first of these is the variable result of the integration and the balance are terms not containing p which we may properly add to the partial integral with respect to p.

We may use the following expression which is equivalent to (14)

$$H = r_0 - A\left[T\int_0^p \left(\frac{dv}{dT}\right)_p dp_T - \int_0^p v dp_T\right]_{p_0T_0}^{pT} + \int_{T_0}^{T} c_{p_0} dT. \tag{16}$$

The value of c_p in terms of c_{p0} is

$$c_p = -AT\int_0^p \left(\frac{d^2v}{dT^2}\right)_p dp_T + c_{p_0}. \tag{17}$$

Values of U, c_v and μ on the same basis as that of the above expressions, are given by expressions already mentioned and use of the above values for H and c_p.

The general expression for entropy (13) expressed in terms of c_{p0} gives

$$\phi = \frac{r_0}{T_0} - \left[A\int_0^p \left(\frac{dv}{dT}\right)_p dp_T\right]_{p_0T_0}^{pT} + \int_{T_0}^{T} \frac{c_{p_0}}{T} dT. \tag{18}$$

This is an expression of the same nature as (14). To sum up the results of this article, we have obtained perfectly general formulas for determination of $Hc_pUc_v\mu$ and ϕ when we have given expressions for volume v in terms of p and T and specific heat at zero pressure c_{p0} in terms of T. By insertion of the particular expressions proposed by Callender, Heck or Goodenough we obtain values for the quantities mentioned which necessarily follow. Some of these have been obtained by Callender, Heck and Goodenough by less direct methods.

Saturation Values from Volume and Specific Heat at Zero Pressure.— From the preceding relations we may deduce values for the saturation region. We must, however, have in addition to our knowledge of gaseous volume knowledge of liquid volume, and of specific heat of liquid along some isobar. That is to say, if we have volume as a function of pressure and temperature for both liquid and gas, and specific heat at some one point of each isotherm for both liquid and gas, we can deduce values of total heat, heat of evaporation, etc., for the entire plane, including the

saturation region. We therefore suppose that we have values of c_p' and v' so that we can obtain values of H', the total heat of liquid, for any value of p and T, by means of either the exact or approximate formula given in the notation, as well as values of ϕ'. We also suppose we have values of c_{p0} and v so that we can obtain H, the total heat of gas, for any value of p and T by means of (14), as well as ϕ by means of (18).

From this knowledge, we will first deduce the " saturation equation " connecting values of p and T at the edge of condensation and evaporation. The application of the relation

$$dH = Td\phi + Avdp$$

to the change from liquid to gas at the constant values of p and T at saturation, gives

$$H - H' - T(\phi - \phi') = 0. \tag{19}$$

All of the functions in this equation are general expressions in p and T, but the equation is only satisfied if p and T are values at saturation. That is, the equation holds for saturation values of p and T, so that it gives a relation which must exist when p and T have saturation values. *It must therefore be the saturation equation* $f(T) - p = 0$. We will later write the equation explicitly in terms of p and T by substitution of the previously given values of H, H', ϕ and ϕ'.

It is to be noted that this equation can be obtained by direct integration of the Clapeyron equation (6). If H, H', v and v' are general expressions in p and T as already discussed, we write (6) in the form

$$AT(v - v')\frac{dp}{dT} - (H - H') = 0. \tag{20}$$

This is an ordinary differential equation in p and T (not a partial differential equation) which is satisfied only if p and T have saturation values, so that it is the differential equation of the saturation curve. It can be integrated in general and the integral obtained turns out to be (19). To integrate (20) we write it in the form

$$\frac{Av}{T}dp - \frac{H}{T^2}dT - \frac{Av'}{T}dp + \frac{H'}{T^2}dT = 0. \tag{21}$$

It is to be noted that, by virtue of (1) and (2),

$$\left(\frac{d\{H/T - \phi\}}{dT}\right)_p = -\frac{H}{T^2}, \qquad \left(\frac{d\{H/T - \phi\}}{dp}\right)_T = \frac{Av}{T},$$

with similar relations between H', ϕ' and v'. It follows that (21) is an " exact differential equation," and the integral given by these relations is (19).

The Clapeyron equation (6) and the general expression of the saturation equation (19) therefore amount to the same thing, and are not independent relations. In the expression (19) H' and ϕ' are general values for the total heat and entropy of the liquid in terms of p and T. However since (19) holds for saturation values of p and T we can use instead the values of H' and ϕ' on the saturation curve, which we call q and n. Hence we may write (19) in the form

$$H - q - T(\phi - n) = 0. \tag{22}$$

This is an alternate form of the saturation equation, useful if we know q and n directly, as functions of T for instance. H and ϕ are as before general expressions in terms of p and T such as given by (14) and (18).

We will next write the saturation equation as an explicit function of p and T, by substituting in (19) for H and ϕ from (14) and (18). We will substitute for H' and ϕ' the exact expressions in the notation. The saturation equation then becomes

$$\begin{aligned} &- r_0\left(\frac{T}{T_0} - 1\right) - A\left[T^2\int_0^p \left(\frac{d\{v/T\}}{dT}\right)_p dp_T\right]_{p_0T_0}^{pT} + AT\left[\int_0^p \left(\frac{dv}{dT}\right)_p dp_T\right]_{p_0T_0}^{pT} \\ &- \int_{T_0}^T (c_p' - c_{p0})dT + T\int_{T_0}^T \left(\frac{c_p' - c_{p0}}{T}\right)dT - A\int_{p_0}^p v'dp_T = 0. \end{aligned} \tag{23}$$

If we may neglect variation of liquid volume, as is the case except near the critical point, the last term becomes $-A(p - p_0)v'$.

An alternate form of this expression of the saturation equation, as well as of all of the preceding equations, may be obtained by substituting the perfectly general form whereby the value of v may be supposed given,

$$v = \frac{RT}{p} - \Delta,$$

where Δ is a small function of p and T, which would vanish for a perfect gas. We may also write

$$\int_{T_0}^T c_{p0}dT = c(T - T_0) + \Delta_1,$$

$$\int_{T_0}^T \frac{c_{p0}}{T}dT = c\log_n\frac{T}{T_0} + \Delta_2,$$

where Δ_1 and Δ_2 are small functions of T which would vanish if c_{p0} (the gaseous specific heat at zero pressure) were constant, and equal to c.

We may also write, following Callender,

$$\int_{T_0}^T c_p'dT = c'(T - T_0) + \Delta_3,$$

$$\int_{T_0}^T \frac{c_p'}{T}dT = c'\log_n\frac{T}{T_0} + \Delta_4,$$

where Δ_3 and Δ_4 are very small functions of T, since c_p', the liquid specific heat at constant pressure p_0, is very nearly constant, and equal to c'.

The saturation equation (23) then becomes

$$ART \log_n \frac{p}{p_0} - A\left[\int_0^p \Delta dp_T\right]_{p_0T_0}^{pT} + (T - T_0)\left\{A\left[\int_0^p \left(\frac{d\Delta}{dT}\right)_p dp_T\right]^{p_0T_0} - \frac{r_0}{T_0} - (c' - c)\right\} - A\int_{p_0}^p v' dp_T + T(c' - c)\log_n \frac{T}{T_0} \quad (24)$$
$$+ \Delta_1 - T\Delta_2 - \Delta_3 + T\Delta_4 = 0.$$

A similar reduction could be made in the previous expressions for H, ϕ, H', ϕ', etc.

For the case of a perfect gas and perfect liquid, all of the Δs would vanish and the saturation equation would reduce to the following form,

$$ART \log_n \frac{p}{p_0} - (T - T_0)\left\{\frac{r_0}{T_0} + (c' - c)\right\} + T(c' - c)\log_n \frac{T}{T_0} = 0.$$

This expression has often been deduced directly from $pv = RT$ and the assumption that specific heat of gas and liquid are constant. It is known to give but a very rough approximation.

The above exact forms of the saturation equation, (23) and (24), are hardly suited to direct computation of numerical values of saturation pressure or temperature. Known values from experiment can however be substituted and seen to satisfy the equation, or the trial and error method could be used. Hence we have a theoretical means of obtaining saturation pressure and temperature from knowledge of volume for both liquid and gas, and their limiting values of specific heat. By insertion of the saturation values thus obtained in the general expressions for total heat of liquid and gas, H and H', we obtain total heat of saturated liquid and gas, q and λ. By finding the difference between them, we obtain r the latent heat of evaporation. We could also obtain r from the same initial data by means of the Clapeyron equation (6). However, we have already found that this is merely the differential equation corresponding to our general saturation equation (19) so the two methods of obtaining r amount to the same thing and are bound to give equivalent results. The two methods of course give a useful check on computation work. r is also $T(\phi - \phi')$ at saturation.

The system outlined above starts with the expression (14) for total heat of gas at any point, and by means of the value of H' the heat of the liquid at any point, gives the saturation equation, total heat of saturated gas λ and of saturated liquid q and latent heat of evaporation r.

We could however start with (14) and experimental values of saturation

pressure and temperature. We also would require experimental values of liquid volume which need not be accurate, however, except near the critical point.

By substitution of the saturation values in (14) we would obtain values of λ. We could obtain values of r by means of (6). Then from the relation $q = \lambda - r$ values of q would be obtained.

Another variation has been used which starts with values of total heat and volume of saturated liquid, the saturation equation and volume of saturated gas. As a result λ is found by adding q to the value of r computed by means of (6). It must agree with the value of λ found by substituting saturation values in expression for total heat of gas.

In each of the above cases the entropy of saturated gas can be found by the same method as used for λ.

A set of values for v, c_p, λ, r and saturation conditions obtained by use of the preceding relations will of course exactly satisfy the Planck equation (9) or (10) as well as the so-called Clausius equation (7).

Callender, Goodenough and Heck Characteristic Equations for Steam.—Callender[1] has proposed a general expression for gaseous volume

$$v = \frac{RT}{p} - \frac{c^0 T_0{}^n}{T^n} + v',$$

where R, c^0 and n are constants.

For $p = 0$ Callender takes c_{p0} and c_{v0} both constant and given by the perfect gas relations

$$\frac{c_{p0}}{AR} = \frac{K}{K-1}, \quad \frac{c_{v0}}{AR} = \frac{1}{K-1},$$

where K is given by the number of atoms in a molecule and is 5/3, 7/5 and 9/7 respectively for 1, 2 and 3 atoms.

As an additional assumption Callender takes in some cases the value $1/(K-1)$ (which is also the value of c_{v0}/AR) for the exponent n in the equation for v. For a triatomic gas such as steam this is 3.5. The liquid volume, v', is taken constant. Callender then deduces values for specific heat, etc., for the particular case of his equation, by special methods suited to the form of his relations. All of the results which Callender thus obtains can be obtained directly from the general formulas preceding, and the substitution of Callender's values of v, c_{p0} and n. Callender shows that the saturation pressures computed from his form of (24) agree closely with Peabody's smoothing of Regnault's experiments. He substitutes these values in his form of (14) and obtains values of λ. By subtracting experimental values of q he obtains values of r. These he

[1] Roy. Soc. Proc., p. 266, 1900.

substitutes in (6) and obtains values of the slope of the saturation curve, $f'(T)$. These should check with values obtained directly from the saturation curve. Callender does not make this check, but the writer has compared with Peabody's first differences and found good agreement.

As stated, Callender bases his work on the assumption that c_p is constant as the pressure approaches zero. Recent experimental work seems to indicate that this is not true owing to dissociation.

Goodenough[1] originally proposed the equation

$$v = \frac{BT}{p} - (1 + ap)\frac{m}{T^n} - c.$$

This was modified somewhat in the later publication.

B, a, m, n and c are constants.

He proposes a variable value for specific heat at zero pressure,

$$c_{p0} = \alpha + \beta T + \frac{\gamma}{T^2}.$$

Goodenough obtains values for the various quantities we have already discussed, by mathematical work suited to his particular case. All of his results can be obtained by the general formulas of the preceding sections. Goodenough did not originally tie up his results with the known saturation values except by showing that the value of c_p computed by inserting the known saturation values in (9) agreed fairly well with the value by direct computation from a formula equivalent to (17). If there had been exact agreement the characteristic equation would have been consistent with the known saturation conditions. Goodenough later at the suggestion of Heck made a similar comparison by means of (6).

Heck[2] has proposed empirical expressions for v and c_{p0} somewhat more complicated than either of the above, but so arranged that there is close agreement with the various experimental values. All of Heck's mathematical work can be carried out by the preceding general formulas.

Van der Waal's equation does not give a simple expression for v as a function of p and T so that it does not readily lend itself to our system of analysis.

Saturation Equation Used Instead of Specific Heat at Zero Pressure.—Up to this point we have supposed that one of the initially given relations in addition to the general value of the volume is the specific heat of gas at zero pressure, and have given the general theory of the particular cases cited by Callender, Goodenough and Heck. We have seen that this leads to an expression for the saturation equation. We now proceed to

[1] Trans. A. S. M. E., Vol. 34, p. 507, 1912. Univ. of Ill. Bull., No. 75, Sept. 7, 1914.

[2] Trans. A. S. M. E., Vol. 35, p. 391, 1913.

give the mathematical theory of a reversal of this method, in which the saturation equation $f(T) = p$, which is well known from experiment, is used as a basis in addition to the general value of the volume; instead of rather arbitrarily assumed expressions for specific heat at zero pressure. This new method has not yet been used for actual computation work.

As already pointed out (14) was derived by using for the initial value of total heat on each isotherm, that occurring where it crosses the isobar $p = 0$. We now use for the initial value on each isotherm that occurring where it crosses the saturation curve, which is itself derived from the value of total heat of liquid at crossing of the isobar $p = p_0$ and values of liquid volume.

We start with values of liquid volume and specific heat of liquid at $p = p_0$. From the relations given in the notation we determine q the heat of saturated liquid. From the general expression for v and the saturation equation and (6) we determine r. By adding q and r we determine λ, the total heat at saturation values of p and T.

We may then express the general integral (11) in the form

$$H = \lambda - AT^2 \int_{f(T)}^{p} \left(\frac{d\{v/T\}}{dT} \right)_p dp_T.$$

As already remarked T is considered constant and left with its general value in the partial integration with respect to p and then the upper and lower limits respectively substituted for p, leaving T as T in both cases.

In actual use of this method it would probably be best to use tables of q, v at saturation, dp/dT, r and λ, all for successively increasing values of T. Then we could make a table of the function $F(T)$ for various values of T from the relation

$$F(T) = \lambda + AT^2 \int^{f(T)} \left(\frac{d\{v/T\}}{dT} \right)_p dp_T.$$

$F(T)$ is then the function of integration in (11) so that we can use (11) to give total heat.

Entropy of gas in general can be found by a similar process. By means of the formula in the notation we can compute n the entropy of saturated liquid, and from r computed as above we can obtain $n + r/T$ the entropy of saturated gas. Then we can express the general integral (12) in the form

$$\phi = n + \frac{r}{T} - A \int_{f(T)}^{p} \left(\frac{dv}{dT} \right)_p dp_T.$$

As in the preceding case we could make a table of the function $G(T)$ from the relation

$$G(T) = n + \frac{r}{T} + A\int^{f(T)} \left(\frac{dv}{dT}\right)_p dp_T.$$

$G(T)$ is the function of integration in (12) so that we can use (12) to give entropy.

Another form in which we could handle this computation of $F(T)$ and $G(T)$ for use in (11) and (12) is as follows.

A table would be made of the auxiliary function y for various values of T from the relation

$$y = A\int^{f(T)} (v - v')dp_T + A\int^{p_0} v'dp_T.$$

By means of a curve, or differences from the table for y, we would next find values of dy/dT and $d(y/T)/dT$. These values could also be found from the following relations, but this would probably be more difficult.

$$T^2\frac{d(y/T)}{dT} = AT^2\int^{f(T)} \left\{\frac{d(\{v - v'\}/T)}{dT}\right\}_p dp_T + ATuf'(T) + AT^2\int^{p_0} \left(\frac{d\{v'/T\}}{dT}\right)_p dp_T,$$

$$\frac{dy}{dT} = A\int^{f(T)} \left\{\frac{d(v - v')}{dT}\right\}_p dp_T + Auf'(T) + A\int^{p_0} \left(\frac{dv'}{dT}\right)_p dp_T.$$

If we may take the liquid volume v' as constant for all values of T all of this work is much simplified.

It then follows that the functions in (11) and (12) are given by the relations

$$F(T) = \int_{T_0}^{T} c_p'dT + T^2\frac{d(y/T)}{dT},$$

$$G(T) = \int_{T_0}^{T} \frac{c_p'}{T}dT + \frac{dy}{dT}.$$

We have also

$$c_p = -AT\int \left(\frac{d^2v}{dT^2}\right)_p dp_T + c_p' + T\frac{d^2y}{dT^2}.$$

From the latter expression we can find the value, previously assumed arbitrarily, of the specific heat at zero pressure, c_{p0}, which follows from the use of the saturation equation. This is done by substituting $p = 0$ in the first integral of the last equation, if our expression for v is valid for such value of p. However our values are legitimate in the finite region even if the values of v and c_{p0} are indeterminate for $p = 0$. For this reason the system of the present section whereby initial values are established by the known saturation condition, is preferable to establishment by the conditions in the mythical region where p is zero.

It is probable that all substances at all temperatures are theoretically gaseous at zero pressure so that every gaseous isotherm crosses the isobar $p = 0$, and so that the assumption of c_p for $p = 0$ theoretically determines the desired initial values. However the volume is infinite, and the number of molecules negligible, and the degree of association of the molecules unknown, and conditions in general so far removed from those with which we usually work, that exterpolation from one region to the other involves considerable assumption.

Volume from Values of Total Heat.—Up to this point we have supposed v given by some sort of characteristic equation and have computed total heat and entropy from it. If, however, we have experimental or other data regarding total heat, we can by a reverse process obtain values of volume.

We do this by partial integration of (4) which gives values of v/T except for an indeterminate function of T referred to later. We must have as a starting point values of $(dH/dp)_T$ for various values of p and T. A general expression for total heat in terms of pressure and temperature, if it existed, would of course give this by direct differentiation. Dr. Davis has also proposed the use of experimental values of μ and c_p and the identity already alluded to,

$$-\mu c_p = \left(\frac{dH}{dp}\right)_T,$$

in conjunction with saturation volumes as discussed below.

As remarked, the partial integration of (4) must be completed by addition of some function of p, arbitrary as far as (4) is concerned, and to be determined by other considerations. (4) gives merely variation of v as T changes for any value of p but gives no information regarding the variation of v with p. We must have, from some other source, a chain of values of v for different values of p, so as to establish one value of v on each isobar. (4) then gives all other values of v on an isobar. Such a series of values would be furnished by the volume of the saturated gas. These could in turn be furnished by the total heat of the gas and the volume of the liquid at saturation. That is, the necessary chain of values of volume could be volumes of liquid if we have total heat and saturation data.

We have as the general integral of (4)

$$v = -JT\int \frac{1}{T^2}\left(\frac{dH}{dp}\right)_T dT_p + T\psi(p).$$

If we have means of determining the saturation volume v_p in terms of pressure we can use the following form of the integral

$$v = -JT\int_{f^{-1}(p)}^{T}\frac{1}{T^2}\left(\frac{dH}{dp}\right)_T dT_p + Tv_p. \qquad (25)$$

This gives volume of superheated gas for any temperature and pressure, where the saturation volume v_p and the lower limit of the integral are values for the pressure in question at saturation temperature.

Obviously we can also obtain total heat from the knowledge already supposed, of values of $-\mu c_p$ which is $(dH/dp)_T$ and c_p which is $(dH/dT)_p$, the value being

$$H = r_0 + \int_{p_0T_0}^{pT} -\mu c_p dp_T + \left[\int c_p dT_p\right]_{p_0}^{p} \text{(terms in } p \text{ only)},$$

or

$$H = r_0 + \int_{p_0T_0}^{pT} c_p dT_p + \left[\int -\mu c_p dp_T\right]_{T_0}^{T} \text{(terms in } T \text{ only)}.$$

From such a value of total heat in general the value at saturation, λ, would be found by substituting saturation values, and the latent heat r would be found by subtracting q, the heat of the liquid given by equations in the notation. These values of λ and r would probably be shown more conveniently by tables than by equations.

The value of saturation volume v_p alluded to above, may be obtained by (6), or must check with (6), using r as above.

LYNN TURBINE RESEARCH DEPARTMENT,
GENERAL ELECTRIC CO.